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CONTENTS

The Anode Layer in the Electrolytic Polishing of Copper. *H. F. Walton*. 219

Improvements in the Electrowinning of Chromium. *R. R. Lloyd, J. B. Rosenbaum, V. E. Homme, L. P. Davis, and C. C. Merrill*..... 227

Gold-Plated Electrode for Measurement of Conductance of Electrolytes. *Sidney Barnartt*..... 235

Technical Reviews

Recent Advances in the Electrochemistry of Membranes of High Ionic Selectivity. *Karl Sollner*..... 139C

Current Affairs

Plans for Buffalo Meeting..... 153C

Fourth Annual Battery Research and Development Conference..... 154C

News Notes..... 155C

Division and Section News..... 156C

Personals..... 158C

New Members..... 158C

Letters to the Editor..... 158C

Notes from Industry..... 159C

Employment Situation..... 159C

Annual Report of the Board of Directors..... 161C

Annual Report of the Secretary..... 161C

Report of Tellers of Election..... 161C

Secretary's Financial Report..... 162C

Treasurer's Report for 1949..... 163C

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Editorial

Government and Education

PRESIDENT SEYMOUR, of Yale University, recently warned privately-endowed universities against dependence on government benefaction. The warning comes at a time when decreasing income from endowments and mounting costs have placed a financial Damocles' sword over practically all private universities. The need for some solution, although not generally desperate now, may soon become so. Tuition has already been increased to the point where the development of talent from the lower and middle classes is discouraged, a situation which can severely handicap this country a few years hence. Of possible help may be increased voluntary support by responsible industries who sense the dependence of their security and the free enterprise system of doing business on the ultimate objectives and accomplishments of the free universities. Another solution is to rely increasingly on grants from government which has the vested authority to tax industry and private citizens for this purpose.

President Seymour believes the latter resort should be avoided. If universities, seeking to maintain their traditional freedom, accept the principle of government support for general academic programs, "our freedom would certainly be crippled," he said, ". . . our independence would disappear. We should lose the quality which makes our contribution valuable."

The warning is validated by experience of the past. Stifling of the universities has been the standard procedure by governments seeking to destroy personal freedom and to regiment industry. The pursuit of truth for its own sake, regardless of where the chips may fall, is a responsibility of the universities, but this is not always an objective of governments anxious to make secure by force their position of power. Academic freedom is ruled out of order.

In times past even the laws of nature were expected to toe the party line. In 1778, a dispute arose among members of the Royal Society of Great Britain as to the form of electrical conductors most efficient for protecting buildings from lightning. Benjamin Franklin had previously recommended pointed lightning

(*Continued on next page*)

rods, a design sanctioned by the Society at large. But after the American Revolution broke out, Franklin was *persona non grata* and some members felt disposed to discount Franklin's scientific discoveries as well as his political beliefs. Among this number was their patron, King George III, who, on learning that an alternate design might substitute knobs instead of points, requested that Sir John Pringle advocate this proposal. The latter hinted that the laws of nature were not alterable at royal pleasure, whereupon it was intimated that a President of the Royal Society entertaining such an opinion ought to resign. Sir John resigned accordingly.

This was not the first instance of arbitrary pressure on scientists nor, unfortunately, was it the last, as Professor Lysenko of Russia found out recently. Were the universities populated with "John Pringles" there would be less fear of lost freedoms. But universities, like business and government, are served by men who may also be fallible when economic and social pressures mount, whatever their source. Eternal vigilance is still the price of liberty.

Will some future President of the United States, perhaps through the Head of the Science Foundation, dictate the laws of nature to which one must subscribe in order to obtain government aid? Will teachers of biology need to follow the party line as in Russia, and will professors of history and economics be told the "facts" they must teach under penalty of censure and dismissal? In a government by dictatorship, recalling events that have occurred in Germany and in Russia, the answer is obvious. In a democracy, however, the hopes and expectations of free men reach higher levels. With unrestricted exchange of ideas, and a lively competition of suggestions from many minds, the final course of action may come more slowly, but it is also more nearly right. Analogous to laws of the plant and animal world, the inbred ideas and motives of the few in a dictatorship have always led to decay and failure, whereas the cross fertilization of ideas and motives from the many leads to vigor, strength, and success. At least this is the American faith. Insofar as we are able in this sense to maintain a truly democratic form of government, perhaps neither the universities nor the industries need be concerned with the ultimate solution of their immediate problems. Of main importance is to guard the heritage of ideas that made this country great.

RECENT ADVANCES IN THE ELECTROCHEMISTRY OF MEMBRANES OF HIGH IONIC SELECTIVITY*

Karl Sollner‡

ABSTRACT

The characteristic electrochemical behavior of membranes, especially their electromotive action, has recently been elucidated on the basis of their being ion exchangers. New methods are developed for the preparation of electronegative, selectively cation-permeable, and electropositive, selectively anion-permeable, membranes of various degrees of porosity, including "permselective" membranes which act in concentration chains as virtually ideal reversible machines for the transfer of ions, either of cations or anions as the case may be. The electrochemistry of these membranes is described in detail. Permselective membranes can be used as "membrane electrodes" for the electrometric determination of the activities of practically all univalent anions and cations, for the study of Gibbs-Donnan membrane equilibria in systems containing only low-molecular-weight strong electrolytes, for the study of mixed electrolyte solutions and many kindred problems, and in various ion exchange processes between solutions.

1. Membranes of Porous Character for Electrochemical Studies

The experimental study of the electrochemical properties and functions of membranes has been retarded in the past by the lack of suitable objects for investigation. Naturally-occurring as well as conventional types of artificial membranes, with rare exceptions only, are neither suitable for strictly physicochemical studies nor desirable as physicochemical tools.

The purpose of this paper is to present, in an integrated form and from a strictly physicochemical point of view, the electrochemistry of some recently developed types of membranes which are suitable for a systematic study of the electrochemistry of membranes and for use as physicochemical tools.

Space does not permit the presentation of a general historical survey of the development of the electrochemistry of membranes (1, 2). Only the broader theoretical background of the present work can be mentioned here: the basic considerations of Nernst on the electromotive action of ions in solution, especially the liquid junction potential (3); Haber's work on chains involving solid electrolytes such as the glass electrode (4); the theory of membrane equilibria by Donnan (5, 6, 7); the classical investigations by Michaelis on the "dried" collodion membranes (8, 9); certain aspects of the theory of the electrokinetic potential; the newer work on the adsorption of ions and on ion exchange; and the highly important work of Teorell (10), and of Meyer and Sievers (11, 12), who proposed the fixed charge theory of electrochemical membrane behavior which will influence in a decisive manner any further work in the electrochemistry of membranes.

In a systematic study of the physical chemistry of membranes it is convenient to distinguish two main classes of membranes, "homogeneous phase membranes" (oil membranes) and "membranes of porous character."

Homogeneous phase membranes exert their typical membrane functions by means of selective, differential solubility. Particles, molecules, or ions which are soluble in an oil phase can penetrate and pass across it. Membranes of porous character act as sieves which screen out the various species of solute particles according to their different size, and, in the case of ions, also according to the sign and magnitude of their charge.

At the outset of our investigations it was decided to use membranes of porous character since they are much more suitable and convenient for experimental work, and can be prepared with a great variety of characteristics.

Membranes of porous character can arbitrarily be classified into two groups: membranes of high porosity, as exemplified by ordinary dialyzing membranes; and "molecular sieve" or "ion sieve" membranes with pores so narrow that different low-molecular-weight species of molecules and ions are retarded to a differential degree in their permeation across them.

Collodion is a particularly desirable material for the preparation of membranes of porous character because of its ready availability and the ease with which sturdy membranes of various degrees of porosity can be prepared. The densest of these membranes having a very low degree of porosity, the so-called "dried" collodion membranes, according to Michaelis act as molecular and ion sieves (1, 8).[1] Collodion membranes also give rise to very pronounced electrical effects. In addition, they can be readily impregnated with foreign substances, such as proteins, dyestuffs, or alkaloids which profoundly change their electrical characteristics. In addition, collodion membranes are nonswelling to a virtually ideal degree: water-wet collodion membranes when transferred to the solution of any strong inorganic electrolyte do not

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[1] The applicability to "dried" collodion membrane of the ion sieve concept was confirmed by crucial electrochemical experiments during the early phases of our work, in refutation of a repeatedly alleged homogeneous phase (solvent) character of these membranes (13, 14).

change their volume to a detectable extent (15, 16). Thus, the complications due to swelling which arise with many other membranes (cellophane, membranes of animal origin, etc.) are absent. For all these reasons and because of their widespread prior use, collodion membranes were chosen as the material for our studies. In conformity with the general purpose of this paper the work on the ion sieve membranes will be stressed here.

The selection of the collodion membranes as the object for our studies, however, should not obscure the fact that collodion membranes in themselves are not of any unique scientific significance. Their real, wider scientific importance is based entirely on the fact that they are excellent and representative objects for the elucidation of the physicochemical nature and of the functional behavior of nonswelling membranes of porous character in general.

II. Fundamental Electrochemistry of Porous-Character Membranes

If a membrane prepared from collodion, parchment, or almost any other material is interposed between two solutions of different concentration of the same electrolyte, an electromotive force arises which is different in most instances from the liquid junction potential originating between the two solutions in the absence of a membrane. The electromotive forces arising in such membrane concentration chains customarily are referred to as "concentration potentials."

The sign and the magnitude of the concentration potential depend on the nature of the electrolyte in the two solutions, on the concentration ratio of the latter, on their absolute concentrations, and finally on the nature of the membrane.

With porous diaphragms and with membranes of highest porosity the concentration potentials do not differ significantly from the corresponding liquid junction potentials. If increasingly dense membranes (of the same material) are interposed between the same two solutions, the concentration potentials deviate more and more from the liquid junction potential.

The direction of the deviation of the concentration potential from the liquid junction potential is closely and invariably correlated with the electrokinetic charge of the membrane. If a membrane with a negative electrokinetic charge is used, the dilute solution is more positive than on free diffusion. If the membrane carries an electropositive electrokinetic charge, the dilute solution is more negative than on free diffusion.

In some instances, with certain very dense membranes, the concentration potential may approach or even reach the so-called "thermodynamically possible maximum value." This is the value of the emf which would arise between the two solutions if they were separated by a phase, for instance a metallic phase, which acts as a pair of reversible electrodes, specific either for the cations or the anions in solution, as the case may be. Thus, the thermodynamically possible maximum value of the concentration potential represents the upper limit of the possible dynamic membrane potentials in concentration chains and the liquid junction potential represents the other limit.

From the formal electrochemical viewpoint the origin of the concentration potentials across membranes of porous character can be explained by the assumption that the virtual transportation of electricity across these membranes is divided between anions and cations in a proportion which is different from the ratio of the transference numbers in free solution of the two species of ions of the electrolyte under consideration (8, 9).

In the case of electronegative membranes, the direction of the deviation of the concentration potential from the liquid junction potential leads to the conclusion that a greater fraction of the current is transported across the membrane by cations than in free solution, in other words, the transference number of the cations in the pores of the membrane (τ_+) is larger than the transference numbers of the cations in free solution, t_+; ($\tau_+ > t_+$ and $\tau_- < t_-$). With positive membranes the inverse holds true. A higher proportion of the current in this case is transported across the membranes by anions than in the adjacent solutions, ($\tau_- > t_-$; and $\tau_+ < t_+$).

Accordingly, it must be concluded that electronegative membranes are preferentially cation-permeable and electropositive membranes preferentially anion-permeable. This conclusion is readily confirmed by observation of the rates of the exchange of ions across the two types of membranes. It is probably the most fundamental fact in the electrochemistry of membranes of porous character.

In formal electrochemical terms the correlation of membrane concentration potential ϵ and the transference numbers τ_+ and τ_- may be expressed by the use of a modified Nernst equation. For the case of a uni-univalent electrolyte, it reads:

$$\epsilon = \frac{\tau_- - \tau_+}{\tau_- + \tau_+} \frac{RT}{F} \ln \frac{a_{\pm}^{(1)}}{a_{\pm}^{(2)}} \qquad (I)$$

where $a_{\pm}^{(1)}$ and $a_{\pm}^{(2)}$ are the activities of the electrolyte in the two solutions, the sum of τ_+ and τ_- by definition being unity.

If an electronegative membrane is exclusively permeable to cations and strictly impermeable to anions, the transference number of the cation, τ_+, is unity, ($\tau_+ = 1.00$; and $\tau_- = 0.00$). A membrane of this nature is said to act as an electronegative "membrane of ideal ionic selectivity." Correspondingly, an electropositive membrane of ideal ionic selectivity is permeable exclusively to anions and impermeable to cations, the transference number of the anion within the membrane being unity ($\tau_- = 1.00$; and $\tau_+ = 0.00$).

The connection between electrokinetic charge of the membranes and their electromotive action has been clearly visualized for a long time. The charges (ions) which form the immovable part of an electric double layer at the collodion-solution interface are attached so firmly to the solid material of the pore walls that they do not participate in the transportation of electric currents across the membranes.

The nearly universal opinion of leading colloid and surface chemists was that the charge of collodion and similar inert materials is due to the adsorption of ions from solution (17, 18). In the early phases of our work we were, therefore, considerably amazed to find the following experimental situation. While collodion membranes prepared from various then-available brands of collodion showed only the smallest differences in their behavior when tested with nonelectrolyte solutions, they showed great and characteristic differences when tested with electrolyte solutions. The electromotive and anomalous osmotic effects described by Michaelis (8, 9) and Loeb (19), upon which we intended to base our further work, could not be reproduced with membranes prepared from the majority of the readily available commercial brands of collodion.

On the basis of the ion-adsorption theory, the differences between the various collodion preparations could be explained only by the assumption that indifferent inorganic ions such as the chloride ion were adsorbed by the vari-

ous preparations to very different degrees. Such an assumption, however, is contradicted by all experience.

It could be demonstrated readily that all the electrochemical properties of collodion (at least in solutions of strong inorganic electrolytes) depend entirely upon the presence of impurities of an acidic nature contained in the collodion (20, 21). The electrochemical structure of collodion is essentially identical with that of materials such as clays, zeolites, or proteins which are customarily classified as *ion exchangers*. The difference between the latter substances and collodion is only of a quantitative nature; potentially dissociable groups are distributed much more sparsely on collodion surfaces than on the surfaces of the other materials.

This concept of the electrochemical nature of collodion links the collodion membranes closely to the frequently used "proteinized" collodion membranes, the outer and inner surfaces of which are covered with adsorbed protein. In both instances the electrochemical character of the membranes is determined by some high-molecular-weight dissociable compounds located on the inner surfaces of the membrane—its pore walls—which in contact with an electrolyte solution act as ion exchangers.

This leads to the presentation of the highly important fixed-charge theory of electrical membrane behavior. The rather elaborate mathematical terms in which this truly fundamental theory was originally presented by Teorell (10) and later in much greater detail by Meyers and Sievers (11, 12) are far too complex to be outlined here; some of its detailed aspects are open to criticism (22, 23). The physical essence of this theory, however, can be stated qualitatively in a simple manner.

The walls of the pores of the membranes carry inherently a definite number of potentially dissociable groups, anionic (acidic) groups, such as carboxyl groups in the case of electronegative membranes, and cationic (basic) groups, such as amino groups, in the case of electropositive membranes. These dissociable groups are an integral, invariable part of the membrane structure. They are compensated for electrically by counter ions of the opposite sign.

In contact with the solution of any given electrolyte the counter ions of these dissociable fixed groups exchange with the ions of the same sign in solution until an equilibrium state is reached. The membranes act as ion exchange bodies.

The ion exchange capacity of the available membranes is small, in most instances so small as to be difficult to determine (23, 24, 25). Therefore, ion exchange under normal experimental conditions readily leads to the situation where virtually all the fixed charged groups are compensated for electrically by the prevailing "critical" species of ions in solution, meaning by the prevalent cation species in the case of electronegative membranes, the prevalent anions in the case of electropositive membranes.[2] The characteristic electrical effects are due to the fact that the fixed ionized wall groups are unable to participate in the transportation of electricity across the membrane. Any current which flows across the membrane is transported by the counter ions of the fixed charged wall groups, and whatever other electrolyte (cations and anions) may be present in the pores. The concentration of this additional electrolyte in the pores depends upon the width of the pores, the charge density on the pore walls, and the concentration and nature of the electrolyte in the surrounding solution or solutions.

In the case of membranes of high and, in limiting cases, of ideal ionic selectivity—more correctly membranes which under a given set of circumstances are of ideal ionic selectivity—the picture becomes fairly simple. The pores are so narrow that the fixed charged wall groups prevent, by electric repulsion, the permeation of any ions of the same sign. The movement of the counter ions of the fixed charged wall groups alone is, therefore, the cause of all the electrical effects observed with these membranes.

This simplified outline of the fixed charge theory needs to be supplemented; a geometric-steric factor has to be considered. The latter invariably is of importance with membranes with a pore width in the ion sieve range (11, 12).

Membranes, without definitely known exception, have a more or less random distribution of effective pore diameters (2, 8, 26, 27, 28). Those pores which are too narrow to admit the prevailing species of critical ions cannot contribute significantly to the electrical membrane effects. For the present purpose such pores can be assumed to be inoperative. Only those pores which admit the critical ions are functioning actively. They represent a greater or smaller fraction of all the pores of the membrane according to the size of the critical ions in solution. The effective size of ions which comes into play here, as demonstrated first by Michaelis and collaborators (8, 9), is closely related to the hydrated ionic size, which is also known to be the determining factor in the rates of diffusion or electrolytic migration of ions.

[2] The term "critical" ions is used to denote the actual or potential counter ions of the fixed dissociable wall groups of a membrane. Ions identical in sign with the sign of the fixed charged wall groups are denoted as "noncritical" ions.

III. Preparation and Properties of Membranes of High Ionic Selectivity—"Permselective" Membranes

Before we turn to the preparation of membranes of pronounced electrochemical properties it seems necessary to enumerate the characteristics which are desirable in membranes intended for extensive studies on the electrochemistry of membranes and for use as physicochemical tools. It will also be advisable to sketch briefly the results of previous experimental work in this direction.

The desirable membrane properties may be listed as follows: (*a*) Membranes should show an extreme degree of ionic selectivity, so that the thermodynamically possible maximum of the concentration potential may be reached even at relatively high concentrations. (*b*) Electronegative, preferentially cation-permeable membranes and electropositive, preferentially anion-permeable membranes should be strictly analogous in their properties in order to facilitate comparison. (*c*) The absolute permeability of the membranes for the nonrestricted, "critical" ions should be high, so that all ion exchange processes across them can occur at a fast rate; this means the ohmic resistance of the membranes should be low. (*d*) The membranes should come readily to equilibrium with electrolyte solutions when immersed in the latter, so that stable, well-defined states (and potentials) may quickly be established across their thickness. This quality obviously is closely related to and part of the problem of their ohmic resistance. (*e*) The membranes should not deteriorate to a significant extent even on prolonged contact with electrolytes. (*f*) The membranes should be mechanically satisfactory, i.e., they should be uniform in thickness (and all other properties) over their whole area and strong enough to stand considerable handling. (*g*) The

membranes should have a well-defined shape, free from kinks and wrinkles. (*h*) The preparation of the membranes should be easy and reproducible.

The best known and most thoroughly investigated *electronegative membranes*, which to a certain degree approach ideal ionic selectivity, are the "dried" collodion membranes of Michaelis and collaborators (8, 9). These membranes were prepared from ether-alcoholic solutions of certain, as we know now, impure brands of foreign collodion by complete evaporation of the solvent. They were used either in the form of rather strong flat sheets of several tenths of a millimeter thickness or in the form of rather thin walled bags, wrinkled and fairly fragile, cast in the conventional way inside test tubes.

Michaelis has characterized these membranes particularly by the measurement of the "characteristic concentration potential" (C.Co.P.), the electromotive force which arises when 0.1*N* and 0.01*N* potassium chloride solutions are separated by a membrane. The values of the C.Co.P. with the best of his membranes varied between +48 and +53 millivolts with occasional values slightly higher (the plus sign indicating that the more dilute solution is positive). The maximum thermodynamically possible value is +55.1 mv. The resistance of these membranes was high, even for fairly thin membranes, of the order of 10^8 ohms per square centimeter in 0.1*N* potassium chloride solutions.

Membranes which are prepared from pure collodion show a C.Co.P. which varies irregularly from +25 to +45 millivolts, and have a resistance in excess of 5×10^8 ohms per square centimeter in 0.1*N* potassium chloride.

Electropositive membranes of low porosity and high ionic selectivity analogous to the dried collodion membranes have been described repeatedly. They are dried collodion membranes impregnated with basic dyestuffs and alkaloids. These membranes have numerous shortcomings. Their ionic selectivity, in most cases, is not entirely satisfactory, and even more important, they are not stable; the membranes partially release the alkaloids or dyestuffs into the adjacent solutions while in use. The absolute permeability of these membranes is extremely low, similar to that of the previously mentioned dried collodion membranes. Dried electropositive protein collodion membranes of high ionic selectivity, which might be satisfactory within narrow pH limits were, apparently, never investigated in detail from the electrochemical point of view.

The fixed charge theory implicitly gives directions towards the preparation of membranes of highest electrical activity. The theory postulates that, *ceteris paribus*, the electrochemical properties of porous membranes will be more pronounced as the number of potentially dissociable groups per unit area on the walls of the pores increases.

For the case of the electronegative (acidic) membranes the results of our work in this direction may be summarized as follows: Collodion can be "activated" by oxidation, for oxidation increases the number of dissociable groups (carboxyl groups) (20, 29). The oxidation may be applied to fibrous collodion as well as to membranes. Sodium and calcium hypochlorite and sodium hypobromite are satisfactory oxidizing agents; most effective, however, are solutions of sodium and potassium hydroxide. Alkalies bring about a complicated decomposition of nitrocellulose with the formation of nitrous compounds, which cause thorough oxidation.

Collodion in bulk, activated in this manner, is electrochemically more active than the impure collodion preparations which were used formerly. The oxidation of collodion membranes, as such, yields still more satisfactory results.

Membranes of high porosity after oxidation show a great increase of the concentration potential. The latter might reach a value ten times higher, and more, than in the unoxidized state. Likewise electro-osmosis through them is considerably enhanced, particularly at higher concentrations (2, 29). Their behavior towards nonelectrolytes is not much changed by oxidation.

For the preparation of "dried" type membranes which show the desired combination of highest ionic selectivity with low resistance, membranes of high porosity are oxidized with sodium or potassium hydroxide and dried over glass mandrels under carefully controlled conditions (30, 31).

A four per cent solution of collodion cotton in absolute ether-alcohol, 50:50, is poured slowly over test tubes while they are rotated in a horizontal position, the test tubes having at their bottom a small hole sealed with sugar. The tubes are covered evenly with collodion without the formation of ridges or thin spots. After three or four minutes another layer of collodion is added, and three to six minutes later a third, the intervals depending on the desired membrane properties. The tubes are rotated for another six to ten minutes and immersed in distilled water. These membranes of high porosity are oxidized in 0.5*N* or 1*N* sodium hydroxide at controlled temperature for a measured length of time, stronger oxidation increasing the activity and reducing the resistance (and also the strength) of the ultimately resulting membrane. After washing, the membranes are dried on the tubes in air of controlled humidity. These dried membranes are removed from the tubes after soaking in water for a few hours. For easy handling, the glass-clear, perfectly smooth membranes are tied with linen thread to glass rings which fit inside their open end. They are stored in distilled water and never allowed to dry while in use. These membranes are sufficiently strong to withstand routine handling in serial experiments without breaking; their electrochemical properties do not change significantly over periods of several months.

The thickness of these membranes is 30–40 μ, their water content by weight 14 to 23 per cent. The characteristic concentration potential across them reaches the thermodynamically possible maximum value of +55.1 mv within the limits of the experimental error. Their absolute permeability is high, depending on such factors as the oxidation time and the humidity at drying. By variation of these factors their resistance in 0.1*N* potassium chloride solution, $\rho_{0.1N\ KCl}$, can be adjusted to 200 ohms per square centimeter and less. Membranes with still lower resistance generally do not yield the highest values of the characteristic concentration potential.

These membranes have been designated as "permselective" collodion membranes.

For the preparation of electropositive membranes we had to rely on the adsorption method since there is no simple way to introduce basic (cationic) groups into collodion by means of a chemical reaction. Protamine, a basic protein with an isoelectric point about pH 12 and a molecular weight of around 3000 was found to be suitable for this purpose (32). It is adsorbed readily and practically irreversibly on collodion.

Protamine collodion membranes of high porosity and great electrochemical activity are prepared by immersing collodion membranes for two days in solutions of protamine sulfate at a pH of about 10.5. These membranes are strongly electropositive in the whole

range from about pH 2.0 to pH 9.6. Thus, they are useful in the neutral range around pH 7, while oxyhemoglobin membranes, the best of the previously described proteinized electropositive membranes of high porosity, are positive only within the range of pH 2.0 to 4.3 (33).

Satisfactory "dried" type protamine collodion membranes can be made in a manner similar to the preparation of the permselective collodion membranes (34, 35).

Three layer collodion membranes of high porosity are immersed for several days in protamine solution buffered at pH 10.5 while still on the tubes. The membranes are washed, dried on the test tubes under controlled conditions, wetted again and removed from the tubes, and finally dried without support for several hours in air of controlled humidity. By this second drying they are shrunk to a barely noticeable extent while their ionic selectivity is raised to a constant and reproducible level.

These membranes, designated as permselective protamine collodion membranes, are mechanically strong and keep their electrochemical properties for at least a year when stored either dry or wet. Their resistance can be adjusted to very low values similar to those of the permselective collodion membranes. The characteristic concentration potential across them is regularly −52.8 to −53.2 millivolts; the thermodynamically possible maximum value of −55.1 mv, however, has never been reached. They are the electropositive analogues of the electronegative permselective collodion membranes except for this slight defect.

Table I shows the progress in the preparation of highly ion selective membranes which results from the new technique of making permselective membranes.

TABLE I. *A comparison of electromotive behavior and resistance of several kinds of conventional ion sieve and of "permselective" membranes*

Description of membrane	Characteristic concentration potential 0.1*N* KCl/0.01*N* KCl	Resistance in 0.1*N* KCl ($\rho_{0.1N\ KCl}$)	Remarks
A. Electronegative membranes			
	mv	*Ω/cm²*	
Impure imported collodion	+45 to +53	~100.000	Not obtainable since 1939. Resistance *cannot* be adjusted at will
Pure commercial collodion	+25 to +45	>500.000	Resistance *cannot* be adjusted at will
Crude collodion	+45 to +50	~100.000	
Oxidized collodion	+50 to +55	>500.000	
"Permselective" membranes	(+54.5 to +55.1) 55.1 ± 0.05	(<100->5000) <200->5000	Resistance *can* be adjusted at will
B. Electropositive membranes			
	mv	*Ω/cm²*	
Dyestuff impregnated collodion membrane	−45 to −52 (drops with time)	>500.000	Unstable; resistance *cannot* be adjusted at will
Permselective Protamine collodion membrane	(−52.8 to −53.2) 53.2 ± 0.1	(<25->5000) <300->5000	Stable; resistance *can* be adjusted at will

IV. The Electrochemistry of Permselective Membranes

This section presents some systematic investigations on the electrochemistry of permselective membranes, beginning with the concentration potential.

The technique used in the measurements of concentration potentials was the conventional one employing the chain: saturated calomel electrode / saturated potassium chloride / saturated potassium chloride agar bridge / electrolyte c_2 / membrane / electrolyte c_1 / saturated potassium chloride agar bridge / saturated potassium chloride / saturated calomel electrode.

The first experimental task was to determine the rate at which final stable potentials across various permselective membranes are reached under different conditions[3] (36, 37). Two fundamentally different cases must be distinguished. On the one hand, one may investigate the time effects which arise if a membrane saturated with critical ions of one type is brought into contact with the solution of an electrolyte having some other critical ion. In this case ion exchange must take place throughout the pore system of the membrane before final potentials can be obtained. On the other hand, the membrane may already have undergone ion exchange with critical ions in solution.

In the former case, in which ion exchange must occur before a final stable state is reached, it takes from several minutes up to several hours before stable concentration potentials are established. Specifically it was found that the final stable potentials are established the more slowly the denser the membranes, the larger the hydrated size of the critical ion, and the more concentrated the solutions. The rate at which the final stable concentration potentials are reached seems to be practically independent of the nature (size and valency) of the noncritical ion (36, 37).

The rates of establishment of the concentration potential across membranes which are already saturated with the critical ion species by prior ion exchange are much higher and less characteristic of the different ions. Final stable potentials are reached in most instances in less than two minutes; adaptation periods of more than 10 minutes are rare. These fast rates are of importance in the practical use of these membranes.

[3] Since the water permeability of membranes of porous character is not zero, a true thermodynamic equilibrium cannot be reached (even with membranes of ideal ionic selectivity) under the experimental conditions which obtain when the concentration potential is measured by the conventional method. For the establishment of a true thermodynamic equilibrium it would be necessary to compensate for the difference in solvent activities of the two solutions by applying a hydrostatic pressure of appropriate magnitude to the more concentrated solution, or to incorporate the proper concentration of a not permeable nonelectrolyte in the more dilute solution. All this, however, is hardly of practical significance with permselective membranes because of their low water permeability. Correct stable potentials are established long before any significant movement of water occurs.

The final, stable concentration potential across a given membrane is a function of the nature, the concentration ratio, and the absolute concentrations of the electrolyte in solution. With the exception of the cases in which ideal ionic membrane selectivity prevails, the selectivity of a membrane in its dependence upon absolute concentration is strictly defined only with concentration ratios which differ infinitesimally from unity. Following an established procedure the concentration ratio 1:2 was used in our experimental work (37, 38).

The significance and the physical meaning of membrane concentration potentials can be visualized by reference to its theoretical upper limit, the calculated potential, E_{max}, which would arise if the membrane behaved under a given set of conditions as an ideal machine for the reversible transfer of the critical ion.

The calculations of the *theoretically possible maximum values of the concentration potential*, E_{max}, are based on the general equation for negative and

$$E_{max} = \frac{RT}{z_+ F} \ln \frac{a_+^{(2)}}{a_+^{(1)}} \qquad \text{(II)}$$

and

$$E_{max} = \frac{-RT}{z_- F} \ln \frac{a_-^{(2)}}{a_-^{(1)}} \qquad \text{(IIa)}$$

for positive membranes respectively. z_+ and z_-, respectively, are the valency of the critical ion. $a_+^{(1)}$ and $a_+^{(2)}$; and $a_-^{(1)}$ and $a_-^{(2)}$ are the activities, $c_+^{(1)}\ \gamma_+^{(1)}$; $c_+^{(2)}\ \gamma_+^{(2)}$; and $c_-^{(1)}\ \gamma_-^{(1)}$ and $c_-^{(2)}\ \gamma_-^{(2)}$. In the case of uni-univalent electrolytes, the mean activity coefficients were used ($\gamma_+ = \gamma_\pm$; $\gamma_- = \gamma_\pm$). With the univalent and bi-univalent electrolytes, potassium sulfate and magnesium chloride, the activity coefficient for the univalent critical ions is calculated assuming that their activities are the same as those of the potassium and chloride ions, respectively, in potassium chloride solution of the same ionic strength.

E_{max} can be calculated with considerable accuracy. The probable error in the case of potassium chloride and lithium chloride is undoubtedly considerably smaller than the accuracy of our experimental determinations. Although the calculated values in the case of potassium sulfate, magnesium chloride, and hydrochloric acid may contain some small systematic error, it seems safe to assume that this error is insignificant compared with the accuracy and reproducibility of the experimental data.

The degree of the ionic selectivity of the permselective collodion membranes is so great and the accuracy and reproducibility of the measured concentration potentials is so high that the experimental data cannot be utilized in full unless corrections are made for the asymmetry of the two liquid-junction potentials, saturated potassium chloride agar bridge / electrolyte c_1; and electrolyte c_2 / saturated potassium chloride agar bridge. All data are corrected, the probable error being about ±0.10 mv, except in the case of the highest concentrations of hydrochloric

TABLE II. *Concentration potentials ϵ (c_2:c_1 = 2:1) of several electrolytes, across a typical permselective collodion membrane and the corresponding transference numbers of the critical and noncritical ions, τ_+ and τ_-*

1	2	3	4	5
Concentration of electrolytes	Theoretical maximum E_{max}	Concentration potential ϵ	Transference number of critical ion (cation), τ_+	Transference number of noncritical ion (anion), τ_-
A. Potassium chloride				
c_2:c_1	E_{max}	ϵ	τ_{K^+}	τ_{Cl^-}
equiv./liter	mv	mv		
0.002/0.001	17.5	17.5	1.000	0.000
0.004/0.002	17.3	17.3	1.000	0.000
0.01/0.005	17.1	17.0	0.997	0.103
0.02/0.01	16.9	17.0	1.003?	0.000
0.04/0.02	16.6	16.6	1.000	0.000
0.1/0.05	16.3	16.1	0.994	0.006
0.2/0.1	16.1	15.2	0.971	0.029
0.4/0.2	16.0	13.9	0.935	0.065
B. Lithium chloride				
c_2:c_1	E_{max}	ϵ	τ_{Li^+}	τ_{Cl^-}
equiv./liter	mv	mv		
0.002/0.001	17.5	17.4	0.997	0.003
0.004/0.002	17.3	17.1	0.994	0.006
0.01/0.005	17.1	16.9	0.994	0.006
0.02/0.01	16.9	16.7	0.994	0.006
0.04/0.02	16.7	16.4	0.991	0.009
0.1/0.05	16.5	15.6	0.973	0.027
0.2/0.1	17.0	14.7	0.932	0.068
0.4/0.2	16.9	13.4	0.896	0.104
C. Potassium sulfate				
c_2:c_1	E_{max}	ϵ	τ_{K^+}	$\tau_{SO_4^{--}}$
equiv./liter	mv	mv		
0.002/0.001	17.4	17.4	1.000	0.000
0.004/0.002	17.1	17.2	1.000	0.000
0.01/0.005	16.9	16.8	0.997	0.003
0.02/0.01	16.7	16.7	1.000	0.000
0.04/0.02	16.4	16.4	1.000	0.000
0.1/0.05	16.1	16.1	1.000	0.000
0.2/0.1	15.9	15.9	1.000	0.000
0.4/0.2	15.8	15.5	0.986	0.014
D. Hydrochloric acid				
c_2:c_1	E_{max}	ϵ	τ_{H^+}	τ_{Cl^-}
equiv./liter	mv	mv		
0.002/0.001	17.4	17.4	1.000	0.000
0.004/0.002	17.3	17.1	0.994	0.006
0.01/0.005	17.1	16.8	0.991	0.009
0.02/0.01	17.0	16.7	0.991	0.009
0.04/0.02	16.8	16.2	0.982	0.018
0.1/0.05	16.8	15.1	0.949	0.051
0.2/0.1	16.8	15.0?	0.946?	0.054?
0.4/0.2	17.6	15.9?	0.952??	0.048??

TABLE III. *Concentration potentials (c_2:c_1 = 2:1) of several electrolytes across a typical permselective protamine collodion membrane and the corresponding transference numbers of the critical and noncritical ions, τ_- and τ_+*

1	2	3	4	5
Concentration of electrolytes	Theoretical maximum E_{max}	Concentration potential ϵ	Transference number of critical ion (anion), τ_-	Transference number of noncritical ion (cation), τ_+
A. Potassium chloride				
c_2:c_1	E_{max}	ϵ	τ_{Cl^-}	τ_{K^+}
equiv./liter	mv	mv		
0.002/0.001	−17.5	−16.4	0.968	0.032
0.004/0.002	−17.3	−16.5	0.977	0.023
0.01/0.005	−17.1	−16.2	0.974	0.026
0.02/0.01	−16.9	−16.2	0.979	0.021
0.04/0.02	−16.6	−15.9	0.979	0.021
0.1/0.05	−16.3	−15.2	0.966	0.034
0.2/0.1	−16.1	−14.5	0.950	0.050
0.4/0.2	−16.0	−13.2	0.913	0.087
B. Potassium iodate				
c_2:c_1	E_{max}	ϵ	$\tau_{IO_3^-}$	τ_{K^+}
equiv./liter	mv	mv		
0.002/0.001	−17.5	−16.2	0.963	0.037
0.004/0.002	−17.3	−16.2	0.968	0.032
0.01/0.005	−16.9	−16.1	0.976	0.024
0.02/0.01	−16.7	−16.0	0.980	0.020
0.04/0.02	−16.1	−14.9	0.963	0.037
0.1/0.05	−15.1	−12.4	0.913	0.087
0.2/0.1	−14.1	−10.2	0.862	0.138
0.4/0.2	—	—	—	—
C. Lithium chloride				
c_2:c_1	E_{max}	ϵ	τ_{Cl^-}	τ_{Li^+}
equiv./liter	mv	mv		
0.002/0.001	−17.5	−16.6	0.974	0.026
0.004/0.002	−17.3	−16.5	0.977	0.023
0.01/0.005	−17.1	−16.6	0.986	0.014
0.02/0.01	−16.9	−16.4	0.985	0.015
0.04/0.02	−16.7	−16.3	0.928	0.012
0.1/0.05	−16.5	−16.2	0.991	0.009
0.2/0.1	−17.0	−16.2	0.976	0.024
0.4/0.2	−16.9	−16.1	0.976	0.024
D. Magnesium chloride				
c_2:c_1	E_{max}	ϵ	τ_{Cl^-}	$\tau_{Mg^{++}}$
equiv./liter	mv	mv		
0.002/0.001	−17.4	−17.5	1.003?	0.000
0.004/0.002	−17.1	−17.3	1.006?	0.000
0.01/0.005	−16.9	−16.7	0.994	0.006
0.02/0.01	−16.7	−16.4	0.991	0.009
0.04/0.02	−16.4	−16.2	0.994	0.006
0.1/0.05	−16.1	−16.0	0.997	0.003
0.2/0.1	−15.9	−16.0	1.003?	0.000
0.4/0.2	−15.8	−16.0	1.006?	0.000

acid. Here the experimental error and the uncertainty of the correction each may be as high as 0.3 mv.

Table II gives for four different electrolytes the experimental and calculated data (t = 25.00°C ± 0.05°) obtained with a typical permselective collodion membrane having a resistance in 0.1N potassium chloride solution, $\rho_{0.1N\ KCl}$, of about 200 Ω/cm². Table III gives analogous data obtained with a typical permselective protamine membrane ($\rho_{0.1N\ KCl}$ = 400 Ω/cm²). In these tables, column 1 presents the concentrations c_2 and c_1 of the electrolyte solutions used in equivalents per liter; column 2 gives for the four different electrolytes the corresponding theoretically possible maximum values of the concentration potential, E_{max}; column 3 presents the corresponding experimental concentration potentials (corrected for the asymmetry of the liquid junction potentials) ϵ; columns 4 and 5 will be explained later and should be disregarded for the moment.

The criterion for the evaluation of these data in terms of ionic selectivity is the difference between the calculated values, E_{max}, and the corresponding experimental concentration potentials, ϵ. The greater the difference between two such corresponding values, the lower is the "ionic selectivity" of a membrane under the particular conditions.

Differences between calculated and experimental concentration potentials up to ±0.20 mv may be due to a combination of limited experimental accuracy and errors in the computation and correction methods used. In the case of the higher concentrations of hydrochloric acid the reliability of the data is considerably lower. All conclusions should be based primarily on the trend of the data over wide concentration ranges.

The data referring to negative and positive membranes will be considered separately.

With the negative collodion membranes (Table II) the agreement between the calculated and the experimental concentration potentials is best with potassium sulfate. Here ideal ionic selectivity within the limits of the significance of the data is observed at all concentrations up to 0.2/0.1N. With potassium chloride, lithium chloride, and hydrochloric acid, these limits are approximately 0.04/0.02, 0.02/0.01, and 0.004/0.002, respectively.

The results with the neutral electrolytes are in best agreement with the theoretical expectation. In the case of potassium sulfate, the bivalent noncritical ion is prevented from penetrating the membrane both on account of its large size and of the stronger electric repulsion which exists between its double charge and the fixed anionic wall groups. With potassium chloride the steric factor does not play an important role, since both ions have very nearly the same hydrated size; only electric repulsion is operative. The greater size of the hydrated lithium ion results in a lower degree of ionic selectivity; some pores which are accessible

on a purely steric basis to potassium and chloride ions are inaccessible to the lithium ion.

The behavior of hydrochloric acid deviates from that of the neutral salts in that the membrane selectivity at medium concentrations is lower than with neutral salts; at the highest concentrations, on the contrary, the selectivity of the membrane with hydrochloric acid appears to be higher than with potassium chloride and lithium chloride.

The results with hydrochloric acid in the middle range of concentration are readily understood on the basis of the fixed-charge theory. In acid solution the surface carboxyl groups are combined with hydrogen ions as counter ions. The resulting free carboxylic acids cannot be expected to act like strong electrolytes; they are dissociated only in part, depending on the pH. The electrochemical structure of the membranes in acid solution differs considerably from that existing, with fair uniformity, in all neutral solutions where the acidic surface groups with their counter ions act as strong, completely dissociated electrolytes (23). A definite explanation of the experimental data at the highest concentrations of hydrochloric acid is still lacking. Most likely they can not be taken at their face value, but are due to a summation of errors.

With the permselective protamine collodion membranes (Table III), the agreement between the calculated and the experimental concentration potentials is best with magnesium chloride; ideal ionic selectivity is approached closely in this case. With the uni-univalent electrolytes, however, an ideal degree of ionic selectivity is not reached in a single instance. Even at the lowest concentrations a considerable difference exists between the measured and the theoretically possible maximum concentration potentials. The membrane selectivity is highest with lithium chloride, less with potassium chloride, and still less with potassium iodate. These differences between the various electrolytes can readily be understood on the same basis as in the case of the electronegative membranes.

The fact that the permselective protamine collodion membranes lack a virtually ideal degree of ionic selectivity even in fairly dilute solutions (except in cases of extreme steric hindrance of an unusually large or polyvalent noncritical ion) is explained by the presence in the protamine molecule of at least one acidic (anionic) group. Accordingly, acidic groups must occupy some decisive spots in the pore system of the protamine membranes: these membranes represent mosaics of numerous selectively anion-permeable pores and a few selectively cation-permeable pores.

It might be added that the concentration range of useful highest ionic selectivity of the permselective membranes can be expanded to chains with one solution considerably more concentrated than those shown in Tables II and III for the 2:1 concentration ratio. This is achieved by keeping the absolute concentration on one side of the membrane fairly low; e.g., 0.01*N* or less, and working with a large concentration ratio, which might be 100:1 or even larger.

This effect, which is of considerable significance in the use of the permselective membranes, can be explained in the following manner. The membranes are relatively thick, about 30 to 40 μ. When one side of a membrane is in contact with a sufficiently dilute solution, an adjacent layer of the membrane is not greatly influenced by the presence of a relatively concentrated solution on the other side of the membrane; this layer, therefore, retains a high degree of ionic selectivity, although the layer of the membrane which is in immediate contact with the more concentrated solution might show a considerably impaired selectivity.

Our work thus far was confined nearly exclusively to systems with univalent critical ions. Many bi- and polyvalent critical ions, e.g., Ca^{++}, Sr^{++}, and Ba^{++} ions give erratic potentials while at least one, Mg^{++} ion, gives reasonable and reproducible potentials (39). There are obviously several fundamental complications. One is that many surface compounds involving bi- and polyvalent critical ions are not completely dissociated; they are, so to speak, "insoluble." This seems to be the case with the Ca^{++}, Sr^{++}, and Ba^{++} salts of "nitrocellulosic acid," the acidic component of oxidized collodion. Another difficulty is the reproducible preparation of membranes which have a sufficient degree of porosity to be permeable to the, of necessity, larger bivalent ions while they are impermeable to univalent noncritical ions exclusively on account of their charge. This latter difficulty, however, has been overcome by the use of carefully selected membranes (39). Membranes which would differentiate sharply between bivalent critical and bivalent noncritical ions might be prepared quite readily.

The data presented in columns 2 and 3 of Tables II and III become fully meaningful from the electrochemical point of view when evaluated in terms of transference numbers with the aid of equation (I). The second term on the right hand side of equation (I) is E_{max}, as can be seen readily by reference to equations (II) and (IIa).

The transference numbers in the membrane of the critical and noncritical ions obtained in this manner are tabulated in columns 4 and 5 of Tables II and III. Deviations of ± 0.003 from unity in the transference numbers of the critical ions cannot be taken as significant, because of the limitation of the experimental accuracy; even deviations of ± 0.006 should be considered significant only with reference to the general trend of the data.

The τ_+ values for the negative membranes, and the τ_- figures for the positive membranes indicate to what extent the membranes under a given set of conditions approach the properties of ideal cationic and ideal anionic conductors.[4]

Electrochemically, the permselective electronegative and electropositive membranes may be considered as new types of cationic and anionic conductors. Within certain limits they behave electromotively like layers of certain solid electrolytes with either anionic or cationic conductance only.[5]

[4] Because of the limited accuracy of the corrected experimental (ϵ) and calculated (E_{max}) data, the degree to which membranes of highest ionic selectivity approach the character of ideal anionic or cationic conductors can be determined with greater accuracy by methods other than direct potential measurements. As such methods one may mention the combination of absolute "leak" and resistance measurements, studies on the transfer of ions in an electric field across the membranes, and studies of both the rates of cation *and* anion exchange across the membranes, carried out preferentially with tracer elements.

[5] There are two fundamental differences between the electromotive action of solid electrolyte interphases and the permselective membranes. In the case of the solid electrolytes, the potential is determined solely by the activity in the adjacent solutions of specific ions, independent, or nearly so, of the presence of other ions. In other words, in mixed solutions the solid electrolyte phases act like specific reversible electrodes. The solid electrolytes have a definite composition which is independent of the presence of other ions of the same or of the opposite sign of charge in the adjacent solution.

Another property of the permselective membranes which is of considerable interest is their resistance in equilibrium with various electrolyte solutions.

The resistance was measured with the test-tube-shaped membranes between two test-tube-shaped platinized platinum electrodes, one outside and one inside of the membrane (31) (T = 25.00°C ± 0.05°C; frequency of the alternating current about 1000 cycles per second).

The bulk of the resistance data which we have available (39) has not yet been analyzed in full. Representative figures for a typical permselective collodion membrane are given in column 2 of Table IV and for a typical permselective protamine membrane in column 3. These data are, of course, only illustrative examples to show the differences between different electrolytes; the absolute resistance of the permselective membrane varies greatly depending on minor details in the method of preparation.

The data of Table IV do not permit more than a few preliminary conclusions: (*a*) The conductance of permselective membranes in solutions of different concentration of the same electrolyte is not proportional to the concentration of these solutions; it is relatively greater at low than at high concentrations, as can be expected on the basis of the fixed-charge theory. (*b*) The influence of the critical ion on the membrane resistance is greater than that of the noncritical ion. (*c*) Bivalent critical ions make for an unusually high resistance of the membranes; these ions are obviously unable to enter many pores of the membrane because of their double charge and their large hydrated size. The high resistance of the protamine membrane in 0.001N magnesium chloride solution is still awaiting a satisfactory explanation.

The resistance of the collodion membranes in contact with hydrochloric acid is not very different from that with potassium chloride in spite of the high migration velocity of the hydrogen ion. This might be explained by the incomplete dissociation of the acidic surface compounds in the membrane.

These results closely parallel, as can be expected, the data on the rate of

TABLE IV. *The electrical resistances of two typical permselective membranes in contact with solutions of several electrolytes at three concentration levels*

1		2	3
Electrolyte solution		Collodion membrane	Protamine collodion membrane
	equiv./liter	Ω/100 cm²	Ω/100 cm²
KCl	0.1	2.3	11.8
	0.01	4.8	39.3
	0.001	17.6	78.3
K_2SO_4	0.1	2.4	363
	0.01	6.1	395
	0.001	32.6	457
K_3-Citrate	0.1	2.0	—
	0.01	4.9	—
	0.001	39.8	—
LiCl	0.1	6.3	16.6
	0.01	11.0	49.8
	0.001	51.3	90.8
$MgCl_2$	0.1	96.1	21.1
	0.01	148	83.3
	0.001	216	353
HCl	0.1	2.5	—
	0.01	5.1	—
	0.001	21.2	—
K-Acetate	0.1	—	63.2
	0.01	—	110
	0.001	—	223
KF	0.1	—	22.5
	0.01	—	67.4
	0.001	—	136

the establishment of final stable concentration potentials.

Closely related to the resistance of the membranes is the rate of ion exchange across them. This rate, under standard conditions, is a convenient measure of ionic membrane permeability; it is also important from the point of view of the use of the membranes in various physicochemical studies.

If an ideally ion-selective membrane separates two solutions of strong electrolytes, only the "critical" nonrestricted ions exchange across the membrane (of course in electrochemically equivalent quantities). In addition, if a membrane is not ideally ion-selective, a "leak" of the noncritical ions occurs.

For the determination of the rates of ion exchange the test-tube-shaped permselective membranes were filled with 25 ml of one electrolyte and immersed in a larger test tube containing 25 ml of some other electrolyte at the same concentration, the two electrolytes having both different cations and different anions. The inside and the outside solutions, brought to the same level by adjusting the position of the membrane, were stirred by streams of air bubbles. After a quasi-stationary state of diffusion across the membrane was set up, the solutions were replaced by fresh 25-ml samples. Thirty minutes later the experiments were stopped, and the solutions analyzed.

Representative results are given in the self-explanatory Tables V and VI. The small percentage leak of the noncritical ion (column 8 of Tables V and VI) is particularly noteworthy.

The nonelectrolyte permeability of the permselective membranes has not been investigated systematically as yet. Sporadic experiments, however, demonstrate that their nonelectrolyte permeability is low. The denser of these membranes which show the highest degrees of ionic selectivity permit the slow permeation of very low-molecular-weight nonelectrolytes only. With membranes of less than optimum ionic selectivity and lower resistance the nonelectrolyte permeability is considerably greater.

The water permeability of the permselective membranes is low, from the practical point of view it is negligible. For example, a solution of 0.2M sucrose was placed inside a membrane with a resistance of about 150 ohms per square centimeter in 0.1N potassium chloride solution. The rate of water movement under these conditions amounted only to 0.01 ml per hundred square centimeters of membrane surface per hour. With membranes of lower resistance the water permeability is correspondingly higher.

A few critical remarks concerning certain shortcomings of the permselective membranes and their possible improvement seems indicated here.

The preparation of the permselective collodion membranes requires more skill, patience, and experience than seems desirable if they are to be widely used; also their mechanical strength, while

With the permselective membranes, however, the situation is different. Here the composition of the potential determining structure is a function of the composition of the adjacent solution. Therefore, in mixed solution the membranes are not specific for the one or the other kind of "critical" ions.

The second fundamental difference between solid electrolyte phases and the permselective membranes is that within the former the potential determining species of ions are not solvated, while they are hydrated in the latter. It is of great importance to keep in mind these differences between solid electrolyte phases and permselective membranes when the physicochemical use of the latter is contemplated.

adequate, should be improved if possible. A more fundamental shortcoming of these membranes, however, lies in their inherent weak acid character. Their fixed dissociable groups are the carboxyl groups of "nitrocellulosic acid" which has hardly a greater acid strength than salicylic acid (25). This, as discussed before, makes the collodion membranes rather sensitive to changes of pH on the acid side of the neutral point where they lose a good part of their characteristic electrochemical properties. Membranes with acid groups of much greater acid strength, such as those of sulfonic acids, would constitute a great improvement. Still more important would be an increase in the number per unit area of the potentially dissociable groups on the pore walls of the membrane structure. This would automatically result in membranes of a higher degree of ionic selectivity at higher concentration levels than is obtainable with the described permselective collodion membranes.

The main shortcoming of the permselective protamine membranes is their unavoidable, inherent leak of (univalent) noncritical ions. Improvements in this direction are likely to result from the blocking by chemical combination of the carboxyl groups of the protamine, or from decarboxylation. To a limited extent this problem has already been solved by (partial) esterification. An increase in the basicity of the fixed wall groups in the positive membranes over that of the amino groups of the protamine would be highly desirable, though it is not as necessary as the corresponding improvement of the negative membranes. The incorporation of tertiary and, much better, of quaternary ammonium bases in the pore walls of the membranes should lead to a satisfactory solution of this problem. As is the case with the negative membranes, the range of high ionic selectivity could be extended to higher electrolyte concentrations if the number of basic groups per unit area on the pore walls were increased.

As these points became apparent in the course of our work we searched for materials other than collodion which might be suitable for our purpose. The obvious choice seemed to be the preparation of membranes from commercial ion exchangers provided the porosity of the material could be adequately adjusted. It is well known that ion exchangers in many instances carry potentially dissociable groups on their pore walls as closely packed as is geometrically possible. However, the ion exchangers which were available commercially before the war did not lend themselves to the preparation of membranes. Anion exchangers (not acid adsorbers) as a matter of fact were not available at that time; they have become obtainable only in the last few years. Several early attempts to secure suitable ion exchange material from manufacturers failed.

Anyone attempting to produce new types of permselective membranes from materials other than collodion should consider carefully the valuable experimental suggestions which are contained in the papers of Meyer and collaborators (11), but much development work might be necessary before membranes with the desired combination of properties can be produced.

During the last year two independent groups of investigators have announced the seemingly successful preparation of membranes of fairly low resistance and highest selectivity from ion exchangers (40, 41). An appraisal of these methods, however, will become possible only after experimental details are available. With the art of making, so to speak, tailor-made ion exchangers developing rapidly, there seems to be little doubt that membranes of highly desirable properties prepared from strong acid and strong base types of ion exchangers will become available in the near future. Such membranes might be destined ultimately to supersede, at least for certain purposes, the collodion base type of permselective membranes.

V. Permselective Membranes in Physicochemical Studies and as Physicochemical Tools

One use of general and practical interest to which permselective membranes may be turned is their application as "membrane electrodes" (39, 42). These membranes by virtue of their ability to act electromotively in the presence of a single species of critical ions like specific reversible electrodes may be used for the electrometric determination of ion activities in single electrolyte solutions. By their use it

TABLE V. *The rate of cation exchange across several typical permselective collodion membranes*

1	2	3	4	5	6	7	8
Resistance of membrane in 0.1*N* KCl	Original solutions		Concentration outside after 30 minutes			Cation exchange after 30 min	Anion "leak"
	Inside	Outside	NH_4^+	Cl^-	$C_2O_4^{--}$		
Ω/cm²	*equiv./liter*	*equiv./liter*	*equiv./liter*	*equiv./liter*	*equiv./liter*	*per cent of possible exchange*	*per cent of actual cation exchange*
220	0.1 NH_4Cl	0.1 KNO_3	0.00180	Not detectable		3.6	Not detectable
80	0.1 NH_4Cl	0.1 KNO_3	0.00522	0.00005		10.4	1.0
50	0.1 $(NH_4)_2C_2O_4$	0.1 K_2SO_4	0.00872		Not detectable	17.4	Not detectable
50	0.1 $(NH_4)_2C_2O_4$	0.1 K_2SO_4	0.0354		0.00058	70.8	1.6

TABLE VI. *The rate of anion exchange across several typical permselective protamine collodion membranes*

1	2	3	4	5	6	7	8
Resistance of membrane in 0.1*N* KCl	Original solutions		Concentration outside after 30 minutes			Anion exchange after 30 min	Cation "leak"
	Inside	Outside	Cl^-	NH_4^+	Mg^{++}		
Ω/cm²	*equiv./liter*	*equiv./liter*	*equiv./liter*	*equiv./liter*	*equiv./liter*	*per cent of possible exchange*	*per cent of actual anion exchange*
990	0.1 NH_4Cl	0.1 KNO_3	0.00070	Not detectable		1.4	Not detectable
50	0.1 NH_4Cl	0.1 KNO_3	0.0239	0.00079		47.8	3.3
50	0.1 $MgCl_2$	0.1 KNO_3	0.0242		Not detectable	48.4	Not detectable
50	0.1 $MgCl_2$	0.1 KNO_3	0.0269		Not detectable	53.8	Not detectable

becomes possible to determine the activities of many ions for which specific reversible electrodes do not exist, as is the case with many anions (F^-, NO_3^-, acetate, ClO_3^-, ClO_4^-, IO_3^-, etc.), or where specific reversible electrodes of the conventional type involve considerable experimental difficulties, as is the case with the alkali and alkalin-earth cations (Li^+, Na^+, K^+, NH_4^+, Mg^{++}, etc.).

With membranes which are already saturated with the critical ions under investigation, activity determinations can be made within a few minutes. Results with an error of less than ±1.0 per cent are obtainable with numerous ions in addition to those mentioned before (37, 39).[6] The method is readily applicable on the semi-microchemical and microchemical level (39).

Extensive theoretical discussions of Gibbs-Donnan membrane equilibria can be found in the literature; their experimental study, however, was confined in the past to systems containing colloidal or semi-colloidal ions as nondiffusible ions, and a few systems in which the ferrocyanide ion acted as nondiffusible ion in conjunction with copper-ferrocyanide membranes-(5, 6, 7, 44). Except for this latter case, Donnan equilibria involving only strong inorganic electrolytes, in which relatively small ions act as "nondiffusible" ions, could not be studied; suitable membranes for such investigations were nonexistent. Now, however, the permselective membranes lend themselves admirably to this purpose (39, 45).

In order to demonstrate the existence of a membrane equilibrium, it is only necessary to test experimentally the classical Donnan equations. If the experimental system is selected so that the diffusible ions A^+ and B^+ have the same activities in solutions of the same ionic strength, then the ratios of the activity coefficients will be unity and one may compare analytical concentrations, c, instead of activities as shown in equation (III).

$$\frac{c_{A^+}^{(1)}}{c_{B^+}^{(1)}} = \frac{c_{A^+}^{(2)}}{c_{B^+}^{(2)}} \qquad \text{(III)}$$

Equation (III) was tested with the same experimental arrangement as described previously for the studies on the rate of ion exchange. Osmotic equilibration was established by the addition of the proper amount of a nondiffusible nonelectrolyte (sucrose) to the more dilute solution. The membrane equilibrium was established in 3 to 24 hours according to the nature (resistance) of the membrane used.

The results of three typical experiments on membrane equilibria across permselective collodion membranes are given in the self-explanatory Table VII.

Preliminary tests have shown that protamine-collodion membranes are also usable for Donnan experiments.

The significance for the physical chemistry of electrolyte solutions, as well as for the study of colloidal systems, of the possibility of the experimental study of membrane equilibria which may involve almost any desired combination of uni-univalent and many combinations of uni-polyvalent strong electrolytes hardly requires any emphasis.

The Donnan equilibrium also furnishes a lead to the solution of an old and vexing electrochemical problem (46). Heretofore, the activities of several coexisting species of ions of the same sign in solution could be determined unequivocally only if specific electrodes, which are lacking for many common ions, could be used. Attempts to overcome this difficulty indirectly, e.g., by "compensation dialysis," have been only indifferently successful (47, 48, 49). The Gibbs-Donnan membrane equilibrium principle, however, permits an exact and general solution of this problem which is not restricted by the lack of specific electrodes. It is based on a consideration of the ion distribution *and* of the concomitant membrane potential (46).

The simplest possible case of a dynamic membrane system with more than one species of potential determining ions, aside from the trivial case of concentration chains with membranes of less than ideal ionic selectivity, is the type of chains in which a so-called bi-ionic potential (B.I.P.) arises (31, 35, 39, 50, 51, 52, 53, 54). It originates across a membrane separating the solutions of two electrolytes at the same concentration with different "critical" ions, which are able to exchange across

TABLE VII. *Gibbs-Donnan equilibria across permselective collodion membranes which involve only strong inorganic electrolytes (The anions are the nondiffusible ions)*

Ratio of volumes of Solution in / Solution out	Solute	Original state millimoles/liter		Equilibrium state				Concentration ratio $\frac{\text{In}}{\text{Out}}$	
				Experimental millimoles/liter		Calculated millimoles/liter			
		In	Out	In	Out	In	Out	Experimental	Calculated
1:1	NH_4^+	20.0	10.0	22.4	7.5	22.5	7.5	2.99 ±0.05	3.00
	K^+	10.0	—	7.4	2.4	7.5	2.5	3.08 ±0.10	3.00
	Cl^-	30.0	10.0	30.0	10.2	30.0	10.0	2.94 ±0.05	3.00
	Sucrose	—	33	—	(33)	—	(33)	—	—
1:1	NH_4^+	30.0	—	22.4	7.5	22.5	7.5	2.99 ±0.05	3.00
	K^+	—	10.0	7.5	2.5	7.5	2.5	3.00 ±0.10	3.00
	Cl^-	30.0	10.0	29.8	10.1	30.0	10.0	2.95 ±0.05	3.00
	Sucrose	—	33	—	(33)	—	(33)	—	—
1:10	NH_4^+	50.2	2.51	37.4	3.79	37.5	3.78	9.9 ±0.3	9.9
	K^+	—	2.56	12.0	1.27	12.7	1.29	9.4 ±0.4	9.9
	$C_2O_4^{--}$	25.1	2.54	24.7	2.53	25.1	2.54	9.8 ±0.2	9.9
	Sucrose	—	39	—	(39)	—	(39)	—	—

[6] It might be added that Marshall and collaborators have used clay membranes (of very high resistance) as membrane electrodes for the determination of the activities of univalent, and in some instances also of bivalent cations (43). The discussion of these very interesting membranes is, however, outside the scope of this paper, since Marshall considers them now rather as solid electrolyte phases than as membranes of porous character.

the membrane, and the same "non-critical" ion species for which the membrane is ideally impermeable.

A satisfactory solution of the long controversial problem of the mechanism of the origin of the bi-ionic potential was recently arrived at by the consideration of the membranes as ion exchange bodies according to the Teorell, Meyer-Sievers fixed charge theory (53, 54). The two exchangeable (critical) species of ions compete for positions as counterions of the fixed dissociable groups of the membrane. The relative abundance of the two species of critical ions in the pores times their diffusion velocities determine their respective contributions toward the virtual transportation of electricity across the membrane, which decide the sign and the magnitude of the B.I.P. Worked out in detail this theory of the origin of the B.I.P. seems to fit all the known experimental data.

The elucidation of the mechanism of the bi-ionic potential is of particular interest in view of the fact that these systems represent one of the simplest possible cases of electromotively-active polyionic membrane systems as they exist universally in living tissues.

The use of permselective membranes for the purpose of the exchange, between solutions, of ions (including the exchange of the ions of water) in preparative chemistry and in industrial operations has not been explored as yet. It might prove to be of great practical significance that the ion exchange operations might be performed between phases of different water activity without a disturbing extent of osmotic solvent movement. Industrial chemists might be interested in the numerous possibilities in this field.

To give just a few examples: The salts of pH sensitive organic acids may be converted into the free acid either by membrane hydrolysis or by dialytic ion exchange against an acid without ever coming into contact with the latter as occurs in precipitation reactions.

The regeneration of certain industrial waste liquids seems feasible. For instance, in the system: fairly concentrated (c_1) solution of sodium sulfate / negative permselective membrane / dilute (c_2) sulfuric acid, ($c_1 >> c_2$), the hydrogen and the sodium ion would exchange across the membrane without significant movement of water. In a counter current system, the result would be a sulfuric acid solution of the higher (useful) concentration, c_1, and a waste solution of sodium sulfate of the lower concentration, c_2.

Nonelectrolytes of medium and even of low molecular weight might be separated from electrolytes by the simultaneous use of both electropositive and electronegative membranes; or electrodialysis might be used for the same purpose in a three-cell outfit with a greatly accelerated speed. Also, the separation of bivalent and monovalent ions of the same sign of charge seems to be a problem of some interest.

The discussion of the application of permselective membranes would be incomplete without reference to at least one case of their usefulness in various model studies of biological significance.

The literature contains a great variety of discussions of the possible or probable role of membranes in many complex *in vivo* processes which involve electrolytes (55). Adequate experimental model studies to test the various theories, however, are extremely rare, primarily due to the heretofore prevailing lack of suitable membranes.

We have just finished the experimental investigation of one such complex model system involving the much discussed situation of a membrane composed of preferentially anion and prefrentially cation permeable parts.

Such so-called mosaic membranes have been shown to be amenable to a quantitative theoretical analysis from the electrochemical point of view provided the membranes are of an ideal degree of ionic selectivity, or nearly so (56). The theory can be based on an imaginary separation of the anion and the cation permeable membrane parts. This results in a ring system which represents an "all electrolytic fluid circuit" ("Flüssigkeitsring") in the sense of Dolezalek and Krüger (57).

The experimental test showed a quantitative agreement with the theoretical predictions with an average error of ±2 per cent (58, 59). This seems to be the first instance in which a complex membrane system was amenable to such quantitative treatment.

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Important Notice to Authors
MANUSCRIPTS FOR FALL MEETING

Manuscripts are now being received for the Ninety-Eighth Meeting of the Society, to be held at the Statler Hotel in Buffalo, New York, October 11, 12, 13, and 14, 1950. To be considered for this meeting, *triplicate* copies of manuscripts or abstracts must be received by the Editor of the Journal *not later than* August 1, 1950. The address is 235 West 102nd Street, New York 25, N. Y.

FUTURE MEETINGS
OF
The Electrochemical Society

Buffalo, October 11, 12, 13, and 14, 1950

Sessions on

Batteries, Corrosion, Electrodeposition, and Electro-Organic Chemistry

Round Table on Electrothermics

Headquarters at the Statler Hotel

* * *

Washington, D. C., April 8, 9, 10, and 11, 1951

Sessions on

Electronics, Electrothermics, Electric Insulation, Luminescence,

Rare Metals, and Theoretical Electrochemistry

Round Table on Industrial Electrolytics

Headquarters at the Wardman Park Hotel

* * *

Detroit, Fall, 1951

Headquarters at the Statler Hotel

* * *

Philadelphia, Spring, 1952

* * *

Montreal, Fall, 1952

Authors are invited to submit papers now for the conventions to be held in Buffalo and Washington. All manuscripts should be submitted in triplicate to the Editor of the JOURNAL, 235 West 102nd Street, New York 25, N. Y. The deadline for abstracts or complete manuscripts for the Buffalo Meeting is *August 1, 1950.*

Current Affairs

To Buffalo in October

This is the year, one in every five or six, when The Electrochemical Society offers members and guests an opportunity to revisit the birthplace of the American electrochemical industry—the Niagara Frontier.

For the old-timers, it is a chance to see what changes have been made during the past few years. For the newer members, it is an opportunity to see plants that represent the latest developments of some of the oldest electrochemical processes.

For all the members, both old and new, there will be a stimulating technical program in the environment that has made the Niagara Frontier justly famous as a center of chemical progress. Symposia are planned on Batteries, Corrosion, Electrodeposition, and Electro-Organic Chemistry, and the Electrothermic Division is scheduling a round-table discussion on electric furnace operation.

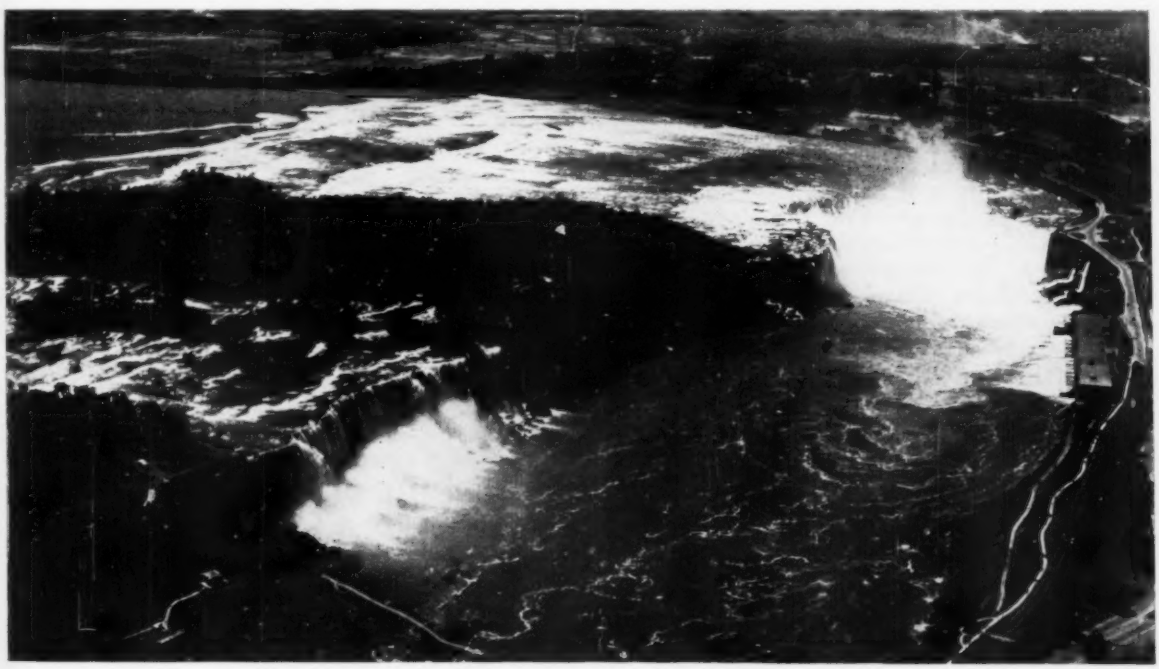
The meeting will offer the ladies several days among the scenic beauties of the Niagara area, with its treasures of history and art, while reviving old acquaintances and making new ones among the increasing number of wives who attend our meetings.

Although arrangements for some of the plant trips are not complete as this is written, we are already assured that the program will include items of general interest as well as of special electrochemical significance.

The local committee has been working for several months on the various features of a program that will make the Ninety-Eighth Meeting another memorable one.

Headquarters will be the Hotel Statler in Buffalo. The dates are October 11, 12, 13, and 14, 1950.

October is still three months away; but at this season the months seem to slip by faster than usual. So before you become so absorbed in your golf game, your garden, or your plans for a vacation trip that you forget it, make a note on the calendar for those four days—*October 11–14*—for the Buffalo Meeting. A similar memorandum in Mrs. Electrochemist's engagement book will make sure that she makes no conflicting dates for either of you.



AIR VIEW OF NIAGARA FALLS—NOTED FOR SCENIC BEAUTY AND AS SOURCE OF ELECTROCHEMICAL POWER

Fourth Annual Battery Research and Development Conference

More than 230 representatives of the battery industry convened at Asbury Park, New Jersey, May 23 and 24, 1950, to attend the Fourth Annual Battery Research and Development Conference, sponsored by the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. The highly successful program, covering latest results in battery research, included papers by the following members of The Electrochemical Society: Ernst G. Baars, Charles H. Clark, A. F. Daniel, Arthur Fleischer, Roy Kirk, Clarence K. Morehouse, Alfred F. Vinal, and Eugene Willihnganz.

New Meteorological Battery

Highlighting the meeting was the announcement by the Signal Corps Engineering Laboratories of the successful development of a meteorological battery capable of powering radio-sonde equipment to heights of over 30 miles into the stratosphere. This new meteorological battery is a magnesium-cuprous chloride reserve type battery which is activated with ordinary tap water just prior to use. Once activated, the battery is capable of operation in ambient temperatures as low as −65°F, temperatures normally encountered in the stratosphere. The new battery replaces the miniature lead-acid battery developed and used extensively during World War II, producing 50 per cent more power and weighing only two-thirds as much as its predecessor. Now being manufactured for the Armed Services, this battery costs considerably less than the lead-acid battery previously used.

Power Sources Branch

The Power Sources Branch, S. C. E. L., is responsible for most of the Government-conducted battery research and development activity. Each year, under the direction of Mr. Grenville B. Ellis, Chief, Power Sources Branch, assisted by Mr. David Linden, Technical Staff, the Laboratories sponsor an industry-wide conference at which the progress on battery research and development is presented to the battery and battery component industry and to interested Government representatives. This conference is the most widely attended of any battery conference; over 125 commercial and Government groups are represented.

Manganese Dioxide

At the morning session on May 23rd, two papers on manganese dioxide were presented. Mr. Charles H. Clark, S.C.E.L, spoke on the Signal Corps manganese dioxide program. The Signal Corps is very much interested in the availability of good battery-grade ores because domestically available manganese ores are generally unsatisfactory for military batteries. An electrolytic method for the production of manganese dioxide from domestic low grade ores has been developed. Use of this ore results in a more than three-fold increase in dry battery capacity. Dr. S. Benedict Levin, S. C. E. L., discussed the six phases or subphases of manganese dioxide that are currently being investigated in order to arrive at a satisfactory and universally accepted method for characterizing these various phases.

Primary Batteries

A number of papers were presented on the primary battery program conducted by the Signal Corps Engineering Laboratories, with particular emphasis on the improvement of the low temperature performance of primary batteries. Mr. Henry Adie, S. C. E. L., described the adverse effects on battery capacity and shelf life resulting from the addition of various contaminants to dry battery components. Dr. Roy Kirk, The Dow Chemical Company, discussed the work conducted during the last year on the magnesium dry cell.

This development was first announced at the Third Annual Battery Research and Development Conference. This magnesium cell, which eliminates the use of zinc, which is in very short supply, also has about twice the capacity of the conventional dry cell. Efforts are now being directed to use this cell in military applications. Dr. Warren C. Vosburgh, Duke University, concluded the morning session with a review of the mechanism of the reactions of the manganese dioxide electrode.

The afternoon session was devoted to a presentation of five papers on the low temperature characteristics of primary batteries. Dr. Alfred B. Garrett, Ohio State University, presented the results of fundamental investigations on electrolytes and electrochemical systems leading to information that can be used in the development of primary batteries which will operate at temperatures as low as −100°F. Polarization studies indicate that six metals show considerable promise for low temperature use in low freezing-point halide electrolyte solutions. These metals are magnesium, zinc, aluminum, tin, nickel, and maganese. Dr. Clarence K. Morehouse, Olin Industries, stated that the capacity at −65°F of non-reserve Leclanché dry cells has been increased so that one hour of operation is now obtained at high current drains. Work is continuing to meet all military performance requirements. Mr. Alfred F. Vinal, National Carbon Division, Union Carbide and Carbon Corporation, and Mr. John J. Murphy, S. C. E. L., discussed the development of the "minimax" and flat cells capable of low temperature performance. Cells have been constructed capable of performance at these extreme low temperatures, but again work is continuing to improve the performance so that military requirements will be met. Mr. Melvin E. Cox, P. R. Mallory & Co., Inc., concluded the first day's activities with a discussion of his experiments with the low temperature alkaline primary cell.

The second session was opened with a discussion of the development of miniature dry cells ranging in capacity from 50 to 150 milliampere hours. Mr. Paul Marsal, National Carbon Division, Union Carbide and Carbon Corporation, and Mr. Hugh M. Morrisin, P. R. Mallory & Company, Inc., discussed their recently initiated investigations leading to the development of a satisfactory military miniature battery.

Special Purpose Batteries

Mr. Fred Hochberg, S. C. E. L., presented a paper on light-weight small size special purpose military batteries being designed by the Laboratories for use with equipment requiring high currents over wide temperature ranges. He described the investigations being conducted with various electrochemical systems giving improved performance

under these very stringent operating requirements and stated that a standard line of "one-shot" batteries is being designed so that military agencies can obtain satisfactory batteries for these special applications on an "off-the-shelf" basis. Mr. Arthur F. Daniel, S. C. E. L.,* presented the paper on the development of the meteorological battery described previously in this article.

Secondary Batteries

The afternoon session on May 24th was devoted to presentation of the results of work on secondary batteries. Dr. L. L. Carrick, University of Michigan, presented his work on the development of a light-weight lead-acid battery. Dr. Eugene Willihnganz, National Battery Company, described his investigations on the development of successful techniques for efficiently charging lead-acid batteries at low temperatures. At the present time, it is realized that the successful use of storage batteries at low temperatures is handicapped by the absence of satisfactory techniques for recharging them at these temperatures. As reported at the Third Annual Battery Research and Development Conference, the S. C. E. L. have developed a lead-acid storage battery capable of discharge at −65°F, but which must be recharged at temperatures above −20°F for successful operation. Dr. Ernst G. Baars, S. C. E. L., and Dr. Arthur Fleischer, Nickel-Cadmium Battery Corporation, concluded this phase of the session with a discussion of the design and development work conducted on sintered plate nickel-cadmium batteries. Experimental batteries will soon be tested by the S. C. E. L. so that the characteristics of the sintered plate nickel-cadmium battery can be fully evaluated.

Mechanical Rectifier

Dr. Otto Jensen, I-T-E Circuit Breaker Company, concluded the Conference with a discussion of the recently developed mechanical rectifier. The mechanical rectifier is primarily a high current, low voltage device. Its greatest use will be where electrical energy is a large item of production cost such as the electrochemical industry or battery industry where its very high efficiency is attractive or as a portable device where its compactness and light weight is of importance.

* * *

Because of their restricted nature, papers presented at the Conference are not available in published form.

New Plant for Potter Instrument

Potter Instrument Company, Incorporated, is transferring its operations to a newly constructed plant at 115 Cutter Mill Road, Great Neck, Long Island. The Company, formerly located at Flushing, New York, manufactures

high-speed electronic counters, precision counter-chronographs, electronic computers, and associated equipment. The new plant, of modernistic design, contains double the floor area of the former location. The sales, research, and manufacturing departments will all be centered at this new location.

Acheson Colloids Opens Pigments Division in N. Y.

The Dispersed Pigments Division of the Acheson Colloids Corporation, Port Huron, Michigan, has opened headquarters at 420 Lexington Avenue, New York City. This is a separate office from the company's Graphite Division at 50 Church Street.

The Acheson firm disperses pigments for paints, coatings, inks, textiles, and other products including plastics. In recent years the company has experimented extensively with colorants and the rapidly growing demand for dispersed pigments in the plastics industry intensified the need for a New York office.

The new division headquarters is headed by George Houston, recently appointed Technical Sales Representative of the Dispersed Pigments Division. Mr. Houston, who has specialized in the study of pigments, coloring, and plastics, will act as liaison between the factory and the field.

Faraday Discussions

A General Discussion on Heterogeneous Catalysis was held by the Faraday Society on April 12–14, at the New Arts Theatre, The University, Liverpool.

The Discussion included about 35 papers, grouped into four Sections, under the following heads:

I. Theories of Adsorption and the Properties of Surface Layers.

II. Adsorption and Catalysis on Metals.

III. Adsorption and Catalysis on Oxides.

IV. Techniques.

Board Requests Use of Official Names of Elements

The Board of Directors of The Electrochemical Society recently voted to recommend for an initial period of one year the official names for fourteen elements unanimously approved by the International Union of Pure and Applied Chemistry at its meeting in Amsterdam last September. The American Chemical Society has taken similar action.

Only two of the new names will be likely to make much difference to American electrochemists. Wolfram is the new official name for tungsten, in agreement with the long used symbol, W. Columbium is no longer correct for element 41; the European name, niobium, and its letter symbol, Nb, have been adopted.

The new names and their letter symbols are tabulated below. Authors of papers submitted to the JOURNAL are requested to conform to the recommended new usage.

Atomic No.	*Symbol*	*New Name*	*Old Name*
4	Be	beryllium	glucinium, glucinum
41	Nb	niobium	columbium
43	Tc	technetium	masurium
61	Pm	promethium	illinium
71	Lu	lutetium	lutecium
72	Hf	hafnium	celtium
74	W	wolfram	tungsten, wolframium
85	At	astatine	virginium
87	Fr	francium	alabamium
91	Pa	protactinium	protoactinium
93	Np	neptunium	
94	Pu	plutonium	
95	Am	americium	
96	Cm	curium	

DIVISION NEWS

Electro-Organic Division

The Electro-Organic Division of the Society will hold a symposium at the Buffalo meeting, October 11–14, 1950. Three papers are currently available for this symposium. Additional papers or abstracts suitable for presentation should be dispatched *promptly* to the Electro-Organic Division in care of the Secretary of the Society, 235 West 102nd Street, New York 25, N. Y.

During past years the Electro-Organic Division has held symposia every two years. It is now contemplated that this schedule will be increased to include an annual symposium to be held at each Fall Meeting of the Society. At the last business meeting of the Division the members present indicated the desirability of this change and decided that the will of the membership of the Division and those nonmembers offering papers would determine the future policy. Papers or abstracts of papers available for presentation at the Electro-Organic symposium should be dispatched promptly, and any comments with respect to the change in policy of the Division will be welcomed by the officers. Papers on the subject of polarography are to be included in the presentations of the Division.

The Electro-Organic Division has nominated the following for election at the Division business meeting in Buffalo next October:

Chairman—H. R. Neumark
Vice-Chairman—C. L. Wilson
Secretary—H. M. Scholberg

As provided by the By-Laws of the Division, additional nominations may be made by petition, signed by five members of the Division, which must be in the hands of the Chairman of the Nominating Committee (N. M. Winslow, National Carbon Company, Cleveland, Ohio) at least ten days before the election.

C. A. Crowley, *Chairman*

Electrothermic Division

Since the 1950 Fall Meeting of The Electrochemical Society will be held in the Buffalo-Niagara Falls area, the Electrothermic Division feels that this would be an opportune time to hold a round-table discussion on electric furnace operation.

The Electrothermic Division normally holds its symposia at the spring meetings, and this practice will continue. Because the Niagara Falls area is the center of electric furnace operation, the Division will sponsor a meeting not normally scheduled.

Mr. George J. Easter, Electro Refractories and Alloys Corporation, of Buffalo, New York, will be moderator of the round-table discussion. The Division feels fortunate in securing Mr. Easter for this role, inasmuch as he has had diverse experience in electric furnace operation as Director of Research of Carborundum Company, and now as Technical Director of Electro Refractories and Alloys Corporation.

A panel of experts prominent in the field will be present at the meeting. The meeting, however, will be informal and off the record, and all those interested in the subject matter are invited to participate in the discussions.

Please contact Mr. George J. Easter, Willett Road, Buffalo 19, New York, for suggestions as to people who would be especially qualified to serve on the question panel, and specific subject matter desired.

Julian Glasser, *Chairman*

SECTION NEWS

Chicago Section

The members and guests of the Chicago Section met on May 5th, at the Chicago Engineers' Club, for a social evening which was very much enjoyed.

A short business meeting preceded the social gathering at which the following officers were elected for the coming year:

Chairman—Paul Leppla
Vice-Chairman—Scott Modjeska
Treasurer—Simon Gary
Secretary—James Conolly

James Conolly, *Secretary*

Cleveland Section

The Cleveland Section's May meeting was devoted to ladies' night. The program included a dinner for the members, their wives, and guests, followed by a theater party. At the latter the group attended the play "Kismet" at the Karamu Theater, a Cleveland institution of widespread fame.

The Section held an election of officers at which the following slate was chosen for 1950–1951:

Chairman—Charles B. Sanborn
Vice-Chairman—Herman C. Froelich
Treasurer—N. C. Cahoon
Secretary—Leo E. Pucher

H. C. Froelich, *Secretary*

Midland Section

The Midland Section of The Electrochemical Society held its third meeting of the season on March 9th at which time Mr. F. L. LaQue of the International Nickel Company gave an interesting and informative talk on "Corrosion."

Mr. LaQue's talk was built around subject matter of direct interest to the local group and produced a large turnout.

The topics covered included the corrosion resistance of titanium, the corrosion and high temperature oxidation resistance of the nodular cast irons, and the corrosion protection afforded by electrodeposits. Potential applications for titanium in chemical process equipment were considered and the corrosion resistance of titanium was compared with that of conventional metals and alloys in a variety of different chemical environments. It was concluded that, for the present, titanium offers no outstanding advantages over the materials currently employed in chemical processing equipment.

The corrosion behavior of nodular cast iron as produced by treatment with magnesium was also discussed. In ordinary soil and water exposures the corrosion rate of nodular cast iron is not appreciably different from that of ordinary cast iron. Nodular iron does, however, exhibit a markedly better resistance to high temperature oxidation. This is attributed to differences in the shape and disposition of the graphite particles in the two types of cast iron.

* * *

The Midland section held its annual "Ladies Night" meeting, complete with dinner and musical entertainment, at the Midland Country Club on April 25th.

Guest speaker of the evening was Mr. E. E. Perrin of The Dow Chemical Company's Public Relations Department who discussed the need for concerted action by business, both large and small, in building better relations with its employees, its stockholders, its customers, and the public at large. It was pointed out that the present trend toward socialism in our Federal Government is a direct measure of the need for improvement in business-public relations and that the problems involved must be faced quickly, squarely, and intelligently if we are to avoid a government-managed economy.

H. A. Robinson, *Secretary*

New York Metropolitan Section

The Spring Meeting of the New York Metropolitan Section took place at the Holley Hotel, New York, on May 17th. A cocktail period and dinner were followed by the annual election of officers. Those elected for the 1950–1951 season are listed below:

Chairman—Harry R. Copson
Vice-Chairman—J. S. Mackay
Secretary-Treasurer—F. A. Lowenheim
Executive Committee—Herbert Bandes, Lyle I. Gilbertson, A. C. Loonam, Martin F. Quaely

At the technical meeting, Mr. Pinckney B. Reed of RCA Engineering Products Department, Camden, New Jersey, discussed a topic of keen current interest: "Industrial Television and Its Applications."

In his speech, Mr. Reed pointed out that the phenomenal growth of one phase of television, home entertainment (which is expected to mean $800,000,000 worth of sets this year), has tended to obscure its fundamental significance as an extension of human sight. This basic function finds expression in "industrial television," a term coined to cover all television applications outside the broadcast field.

There are many potential industrial applications of television. Among these is the use of television in factories and laboratories for monitoring processes, inspection, and centralized supervision. Industrial television may become the expendable eye that can watch dangerous industrial and scientific operations, such as jet engine testing, explosive manufacturing, and chemical processes which are unsafe for a human observer.

At the Weirton Steel Company, television has been used to effect more precise observation and control of a crucial step in the electroplating of tin. Recent tests made in observing melting operations at the Corning Glass Works indicated the usefulness of television in quality control and efficiency.

Future possibilities of industrial television also include such uses as: the inspection of the underside of industrial products, moving trains, and the interior of large products such as cylinders and tanks. It will facilitate observation of the inside of oil well casings, factory chimneys, grain elevators, and other inaccessible areas. Also included are such applications as comparison of the television image with a standard, either optically or electronically, for purposes of product inspection and registration of materials with respect to each other. Visual details presented electronically by the television camera can be made to operate automatic controls or indicators. The ability of television to detect infrared and ultraviolet radiations associated with some industrial and scientific processes, but invisible to the human eye, offers still further possibilities, as does the adaptability of the new small industrial television equipment to looking directly into the eye-piece of the light microscope and reproducing a magnified image on the television screen.

The speaker emphasized cost as the first consideration in designing industrial television equipment: initial cost and lost cost of operation and maintenance as compared to presently available television equipment.

Important design factors are compactness, weight, simplicity of operation and maintenance, and reliability. This includes being unaffected by wide ranges of temperature, weather, smoke, fumes, and other normal industrial conditions. The camera must operate without attendance or critical adjustment. Performance must be on a par with broadcast television. In some applications such as surgery and certain chemical processes, color will be required for maximum effectiveness, but the large majority of industrial applications will be served adequately by the lower cost black and white television.

In anticipating the needs of industry, RCA has developed a new pickup tube called the Vidicon. The tube is one inch in diameter and six inches long and uses the principle of photoconductivity rather than photo-emission as formerly employed in tubes of this type.

The Vidicon has made possible a television camera only 10 inches long, 3 inches wide, and 5 inches high, weighing 8 pounds. The complete system for one camera consists of the camera and a master control monitor unit weighing only 58 pounds.

The lecture was followed by a demonstration of the new equipment.

J. S. Mackay, *Secretary-Treasurer*

Philadelphia Section

The final meeting of the 1949–1950 year of the Philadelphia Section was held May 20, 1950, in the lecture hall of the Chemistry Building, Swarthmore College. A dinner at the Bond Memorial Building, Swarthmore, preceded the meeting. Thirty-nine members and guests, including wives, attended the dinner. Professor Creighton was host to the Section at Swarthmore.

The meeting was called to order by Chairman Osol and the following officers were re-elected for the 1950–51 year:

Chairman—Arthur Osol
Vice-Chairman—John F. Gall
Treasurer—George F. Temple
Secretary—J. F. Hazel

Mr. John J. Rheinfrank of the Graphic Arts Division of the Battelle Memorial Institute delivered the address of the evening on the subject of "Xerography." The lecture was illustrated brilliantly with a moving picture, slides, and demonstrations.

The name Xerography is derived from Greek words meaning *dry writing*. In practice the term applies to the new, dry method of photography which can be used for either graphic reproduction or for duplicating. Advantages are the speed with which prints can be made, the fact that the plate is not expendable and that the operation represents a positive to positive cycle.

Important features are a metallic plate coated, by vacuum distillation, with a photosensitive material such as selenium or anthracene; a device for spraying electrical charges on surfaces and usually consisting of a corona discharge tube; solid powders which are held by electrostatic forces to the surfaces.

A xerographic cycle consisting of the following steps was shown in a moving picture and, except for the first step, demonstrated by the speaker.

(1) Preparation of the plate (this can be used over again).

(2) Sensitization of the plate by spraying electrical charges over it.

(3) Exposure of the plate. A latent image was produced. The charges were drained off from the other areas by grounding, hence solid powders subsequently adhere electrostatically only to that part of the plate which delineated the image.

(4) Transfer of the image to paper or other surface by imparting a charge to the latter.

(5) Heating mildly to fuse the image (powder) to the surface.

Mr. Rheinfrank displayed slides which gave potential applications, e.g., reproductions can be made in colors and on various surfaces such as paper, glass, ceramics, plastics, cloth, wax and metals. Data on electrical charging of dielectric films concluded the interesting address.

J. F. Hazel, *Secretary*

PERSONALS

CHARLES H. POINTER has returned to the School of Chemistry, Metallurgy, and Ceramics at the University of Alabama. Mr. Pointer had been attached to the Naval Air Station, Warrington Branch, at Pensacola, Florida.

ERNEST S. NOSSEN, consulting chemical engineer, formerly executive staff member of the Royal Sulfuric Acid Corporation and its subsidiaries in Amsterdam, Holland, has been appointed Vice-President and Director of Research of E. S. Nossen Laboratories, Inc., in Paterson, New Jersey. The firm specializes in laboratory and pilot-plant work in ore treatment, particularly manganese, batteries, raw materials, and de-ionization and decolorization of liquids.

MARC DARRIN was recently made Associate Director of Research at the Mutual Chemical Company of America in Baltimore, Maryland. Mr. Darrin had previously been Chief Research Chemist with this company.

R. B. HOXENG, Department of Chemistry and Chemical Engineering, Case Institute of Technology, Cleveland, Ohio, will be in charge of a short course in Corrosion to be given at Case Institute in September, 1950.

NEW MEMBERS

In May, 1950, the following were elected to membership in The Electrochemical Society by the Board of Directors:

Active Members

STANLEY M. THURLOW, R. B. Davies Pty., Ltd., 450 Illawarra Rd., Merrickville, N.S.W., Australia (Theoretical Electrochemistry, Corrosion, Electrodeposition, Electrothermics, Electronics, Dielectrics, and Power)

HERBERT L. BARNEBEY, Chemical Plants Division, Blaw-Knox Construction Company, 321 Penn Avenue, Pittsburgh 22, Pennsylvania (Industrial Electrolytic)

JOHN J. CHAPMAN, Institute of Cooperative Research (Johns Hopkins University), mailing add: 5944 Kavon Avenue, Baltimore 6, Maryland (Electric Insulation)

HENRI PRUD'HOMOZ, Fabriques Réunies deLampes Électriques, mailing add: 17 rue Dr. Jacquemaire-Clémenceau, Paris XV, France (Electronics and Industrial Electrolytic)

DAVID H. KENNY, General Motors Research, mailing add: P.O. Box 188, North End Sta., Detroit 2,Michigan (Corrosion and Theoretical Electrochemistry)

ERNEST L. KOEHLER, Armour Research Foundation, mailing add: 5311 Fullerton Avenue, Chicago 39, Illinois (Corrosion)

CHARLES T. LATTIMER, C & P Laboratory, RCA Victor Division, Marion, Indiana (Electronics)

HARRY V. POCHAPSKY, The Cleveland Graphite Bronze Company, mailing add: 24961 Euclid Avenue, Euclid 17, Ohio (Electrodeposition)

HUGH W. SALZBERG, Hunter College, mailing add: 45 Christopher Street, New York 1, New York (Corrosion)

EDWARD S. SHANLEY, Buffalo Electro Chemical Company, mailing add: 369 Southwood Dr., Kenmore 23, New York (Theoretical Electrochemistry)

HENRY J. VYHNALEK, Cleveland Electric Illuminating Company, mailing add: 4418 Bridgeview Avenue, Cleveland, Ohio (Corrosion and Electric Insulation)

ERNEST B. YEAGER, Dept. of Chemistry, Western Reserve University, Cleveland 6, Ohio (Theoretical Electrochemistry)

Reinstatement

FRANCISCO H. LAVAT, Mier y Pesado, 227-E Col. del Valle, Mexico, D.F., Mexico (Theoretical Electrochemistry and Electrodeposition)

Associate Member

ARNOLD D. ARNAUT, Sylvania Electric Products, Inc., P.O. Box 6, Bayside, New York (Electronics)

Student Associate Members

ARTHUR L. GEARY, Room 8-206, Massachusetts Institute of Technology, Cambridge 39, Massachusetts (Corrosion)

ROBERT S. KARPIUK, Dept. of Chemistry, University of Michigan, Ann Arbor, Michigan (Corrosion, Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

ANNOUNCEMENT FROM THE PUBLISHERS

NEW DEVELOPMENTS IN FERROMAGNETIC MATERIALS by J. L. Snoek (N. V. Philips Gloeilampenfabrieken, Eindhoven, Netherlands). Published by Elsevier Publishing Company, Inc., New York, 1949. 150 pages, $2.75.

This book is particularly interesting in the theoretical approach in which the statics and dynamics of ferromagnetism have been developed. About one half of it is devoted to the development of nonmetallic magnetic materials. Contents: I. States of Ferromagnetism, II. Dynamics of Ferromagnetism. III. Development of Magnetic Materials.

LETTERS TO THE EDITOR

Dear Sir:

I believe that attention should be called to the poor quality of the presentation of papers at our Conventions. One of the sessions I attended at the recent Cleveland Meeting ran as much as forty-five minutes late, principally because one or two speakers had been allowed to exceed their allotted time by as much as 100%. If it had not been that other speakers more considerate of their audience curtailed their talks, the session might be going yet.

This situation is far more serious today than it was before the Society began to run parallel sessions. Some members wish to sit in at papers in different rooms, and when the sessions are allowed to get very far off schedule, it becomes impossible for guests to plan their listening.

As has been pointed out many times before, allowing speakers to run overtime is also unfair to those who are scheduled later on the program, for sooner or later the chairman wakes up and decides that things are out of hand with the result that the last few papers on the program have to be rushed through and discussion is cut off.

This situation can be remedied. Authors should be told that oral presentation of a paper is not the same thing as publication, and that it is impossible to present all the many details which will appear in the final publication. They should also be encouraged to follow the excellent example, introduced to this Society by Dr. Holt of the University of Wisconsin, of putting most of

their talk on slides. Finally, if none of these measures succeeds it will be necessary to be ruthless; the chairman must exert his authority and simply tell the author to sit down.

If some of the above suggestions are followed, I am convinced that our meetings, already among the most enjoyable of those of any technical society, will become even better.

F. A. Lowenheim
Rahway, New Jersey

* * *

Seinerhochwohlgeboren

Herrn Prof. Dr. H. H. Uhlig
Redakteur m.b.H.
Journal of The Electrochemical Society
New York, N. Y.

Sir:

Ich will nicht biefen, aber meine Ueberspannung hat geschneppt; wer ist denn eigentlich dieser "Ed.," der den Nerf hat, meine gute Arbeit mit seinen Futtnots und Weisskrecks aufzulausen? "Mal y pense" mein Ei! Ich glaube dieser Offisboi ist selbst zu gross fuer seine Britsches; besser, er stickt zu seinem Bruhm, oder ich komm' und sticke ihn mit seinem eigenen Bollpeunt bis er Onkel skriemt.

Diese forenne Lengwitsches braucht man ja ueberhaupt nicht, wenn man ein gutes Vokabularium [*sic*] hat, wie zum Beispiel mit dem Onkel Fritz, weil er in Manila war, und eines Tages auf der Striet e' Gejammer und e' Geschrei hoert. Es waren naemlich zwei Leimtschusser Missionaris aus Indien, Mann und Frau, in einer Carromata (Spanisch fuer "zwei-Wiel Boggi") in e' Feit mit dem Cochero (Dreifer); sie heult und er kosst; sie sind auf einem Robberneck-tour und haben den Weg verloren; ihr Stiehmboot seelt in e' Viertelstunde und der Boi will sie nicht zurueck an die Bietsch dreifen- sie haben ihm die Sache ueber und ueber explehnt, in Pitschinenglisch und in sieben Indierdialekte, aber er sagt immer blos "no sabe"; kann niemand helfen? Und der Onkel (der selbst nur e' Koppel Fremdwoerter hat):

"Cochero, sabe Pier feif?"

Der: "Si Señor" (Schur Meik).

Onkel F.: "Bueno, sigue pronto!" (Biet es.)

Und der Cochero schwingt die Wipp, und sein zwei-Bitt Poni ist ab wie e' Schuss, und die Missionaris hollern tausend Tenks und Gottblessjuh. Aber der Tscharli Faust meint, das ist alles Nonnsenns, die Forrenners koennen schon ganz gut Englisch unterstehen, wenn man laut genug schautet.

Doch wieder zurueck zu diesem "Ed." Bis der gefeiert ist, schreibe ich ueberhaupt nicht mehr,—zuhellmit es!

Hochachtungsvoll,
Sol Neman

NOTES FROM INDUSTRY

Products

Quality Control Indicator is the name of a new device announced by General Electric Company, Schenectady, aimed to assure the highest possible quality of most mass-produced items and to reduce manufacturing costs at the same time. An electric computor, this instrument keeps an automatic, continuous check on reject rates in manufacturing, and makes possible the location and remedy of abnormal production difficulties as quickly as they occur. The speed with which the indicator works accounts for its increased efficiency.

Clark Electronic Laboratories, Palm Springs, California, are offering a new water cooled selenium rectifier for the chemical industry. These units

are unaffected by corrosive fumes or high ambient temperature and the rectifier plates are sealed against dust. Because of its construction there is little danger of damaging the CELAB units by over heating. They are made in sizes from 1000 to 50,000 amperes in all voltages.

Publications

Fisher Scientific Company has issued a new four-page folder describing recent improvements made in the Gram-atic Balance. The balance is of the one-pan type, and permits accurate analytical weighings to the fourth decimal place in 20 seconds. For folder, write Fisher Scientific Company, 717 Forbes Street, Pittsburgh 19, Pennsylvania.

Schaar and Company, Chicago, has published a new comprehensive catalog of apparatus and equipment, primarily for use in chemical and biochemical

laboratories. Catalog No. 50, "Selected Laboratory Equipment," is alphabetically arranged with occasional functional groupings such as Biochemical, Petroleum, etc. Copies are now available on request.

Manual of Electric Instruments, in a new revised edition, has been announced by the General Electric Company. The new edition describes the fundamentals of construction and operating principles of all major types of electric instruments. It also explains essentials of thermocouples, synchroscopes, frequency meters, electric telemeters, etc. For use in schools and industry, the manual contains 13 chapters, 150 pages, extensively illustrated. Priced at $1 a copy, it may be obtained from the General Electric Company, Schenectady 5, New York.

EMPLOYMENT SITUATION

Metallurgist, B. S. (Chem.), postgraduate work in metallurgy. Research and process development experience in the application of leaching, furnace, and electrolytic methods to the recovery of and refining of copper, lead, tin, silver, cadmium, and other nonferrous metals. Experience, metal powders. *Reply to Box 340.*

THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society is an international organization of individuals and companies concerned with or interested in Electrochemistry and allied subjects.

The Society is dedicated to the advancement of the theory and practice of Electrochemistry and related subjects, as shown in the following divisions:

Battery	Electro-Organic
Corrosion	Electrothermic
Electric Insulation	Industrial Electrolytic
Electrodeposition	Theoretical Electrochemistry
Electronics	

Among the means to this end are the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem appropriate, and cooperation with chemical, electrical, and other scientific and technical societies.

It is an incorporated society without capital stock. The affairs of the Society are managed by a Board of Directors under a Constitution and By-Laws. Officers are nominated by a nominating committee appointed by the Board of Directors and elected by the members.

Direct all general correspondence and inquiries regarding membership to Society headquarters at 235 West 102nd Street, New York 25, N. Y., c/o Mr. W. J. Holian, Assistant Secretary.

Officers of the Society

President ..... CHARLES L. FAUST
Past President ..... ALFRED L. FERGUSON
Vice-President ..... RALPH M. HUNTER
Vice-President ..... J. C. WARNER
Vice-President ..... ROBERT J. MCKAY
Treasurer ..... E. GIDEON WIDELL
Secretary ..... HENRY B. LINFORD

Annual Report of the Board of Directors

During the year of 1949, 13 meetings of the Board of Directors or its executive committee were held. Full details of the business transacted at these meetings are contained in the minutes of the meetings on file in the Secretary's office, where they may be consulted by any member of the Society. Only the important items of business transacted during the year of 1949 are detailed here.

Several major changes of policy were made during the past year. The first dealt with our publication. Plans were formulated to have the JOURNAL printed in a new format, size 8¼ x 11¼ inches, beginning January 1, 1950. At the same time, the publishing of the TRANSACTIONS in separate volumes was discontinued; in the future, proceedings of the semi-annual meetings and discussion of papers will be contained in the JOURNAL. A bound volume containing the 12 issues of the JOURNAL will be made available to members each year at a minimum cost. The necessary actions were taken for the JOURNAL to start accepting advertising on January 1, and, in further support of this, Mr. Raymond G. Ellis was employed as advertising manager on October 17, 1949.

The second major change in policy dealt with membership. Effective January 1, 1950, active membership in The Electrochemical Society was restricted to those individuals possessing certain professional qualifications. The classification of associate membership was created in order to accommodate those who do not yet meet the professional requirements for active membership, and the grade of student associate membership was instituted to give students of electrochemistry in the various universities a better opportunity to participate in the affairs of the Society, thereby stimulating a wider interest in The Electrochemical Society.

The Board of Directors approved a petition from a group of members of the Society living in the Washington, D. C., area to form a Washington-Baltimore Section of The Electrochemical Society.

The Board welcomes the following corporations as Sustaining Members: Potash Company of America, Carlsbad, New Mexico, and National Battery Company, Gould Industrial Division, Depew, New York.

The Young Author's Prize of $100 and the Turner Book Prize were both awarded to Michael A. Streicher. Massoud T. Simnad was appointed Weston Fellow for the year 1949, continuing his studies at Carnegie Institute of Technology.

The following budget for the year 1949 was approved:

Estimated Receipts

Membership Dues	$25,000
Sustaining Membership Dues	5,500
Sales of Publications—Misc.	5,000
Sales of TRANSACTIONS	6,000
Sales of "Modern Electroplating"	850
From Conventions	800
Total	$43,150

Estimated Expenditures

Cost of JOURNAL	$15,000
Salaries	14,000
Cost of Bound TRANSACTIONS	3,800
Stationery	1,000
Office Rent	1,380
Postage	1,000
Allocations to Local Sections, Divisions, and Publication Committee	750
Conventions—including Programs	1,000
Telephone	300
Auditor	150
Young Author's Prize	100
Miscellaneous—inc. Office Supplies	1,000
Total	$39,480

Annual Report of the Secretary

At the completion of the term of office of Dr. R. M. Burns, the Secretary's office was continued in the same location and with approximately the same personnel for the remainder of the year.

In Volume 95 of the JOURNAL (and TRANSACTIONS), there are 32 papers. Most of these papers were presented before the symposia on the following subjects: luminescence, rare metals, and theoretical electrochemistry. Volume 96 contains 36 papers. Most of these were presented in symposia on corrosion, electro-organic chemistry, and electrodeposition.

Report on Membership for 1949

Membership as of January 1, 1949	1,801	
Qualified as members in 1949	178	
Reinstated members	10	
		1,989
Deaths during 1949	9	
Members dropped in 1949 and resignations	98	107
Membership as of December 31, 1949		1,882
Net increase		81

Composition of Total Membership January 1, 1950

Active	
United States	1,624
Canada	58
England	43
India	19
Other Foreign	138
	1,882
Emeritus	32
Honorary	8
Sustaining	57

Report of Tellers of Election

For President: Charles L. Faust, 693; scattered votes, 6; abstentions, 7.

For Vice-President: Robert J. McKay, 368; O. W. Storey, 325; scattered votes, 3; abstentions, 10.

Signed: E. K. MacMahon, *Chairman*
Robert V. Jelinek
Herbert P. Dengler
Tellers of Election

The Tellers' Report was unanimously accepted and President Ferguson declared the candidates C. L. Faust (President) and R. J. McKay (Vice-President) duly elected.

UMI

Secretary's Financial Report

FOR THE YEAR 1949

As Audited by Mr. H. K. Leicht, 463 West Street, New York, N. Y.

BALANCE SHEET

December 31, 1949

Assets		*Liabilities, Reserves, and Surplus*	
Furniture and Office Equipment	$ 1,917.91	Federal Income Tax Withheld	$ 488.60
Cash	20,477.55	Prepaid Sustaining Memberships	500.00
U. S. Savings Bonds (Cost)	39,960.00	Life Memberships	1,683.62
Inventory—Bound Volumes	5,751.60	Prepaid Volumes (Unpublished)	6,641.32
Accrued Income on Investments	2,569.00	Reserve for Depreciation	197.47
		Surplus	61,165.05
Total	$70,676.06	Total	$70,676.06

CASH STATEMENT

January 1 to December 31, 1949

Book balance December 31, 1948		
National City Bank		$21,145.55
Receipts—Jan. 1 to Dec. 31, 1949	$56,663.84	
Disbursements Jan. 1 to Dec. 31, 1949	67,892.05	
Excess disbursements over receipts		$11,228.21
Book balance December 31, 1949		$ 9,917.34
New York Savings Bank		
Transferred from National City Bank—1949	$ 5,000.00	
Interest	49.28	
Book balance December 31, 1949		$ 5,049.28
Dry Dock Savings Institution		
Transferred from National City Bank—1949	$ 5,000.00	
Interest	16.66	
Book balance December 31, 1949		$ 5,016.66
Corn Exchange Bank Trust Company		
Book balance December 31, 1948		$ 324.20
Receipts Jan. 1 to Dec. 31, 1949	$24,184.12	
Disbursements Jan. 1 to Dec. 31, 1949	24,029.26	
Excess receipts over disbursements		154.86
Book balance December 31, 1949		479.06
Cash on hand—Agent		15.21
Total Book Balances and Cash on Hand Dec. 31, 1949		$20,477.55

Book balances and cash on hand Dec. 31, 1949 accounted for as follows:	
National City Bank	$ 9,917.34
New York Savings Bank	5,049.28
Dry Dock Savings Institution	5,016.66
Corn Exchange Bank Trust Company	479.06
Cash on hand—Agent	15.21
Total	$20,477.55

Agent's Account—Corn Exchange Bank Trust Company Dec. 31, 1949	
In bank book balance	$ 479.06
Cash on hand	15.21
Voucherable items	2,501.90
Authorized Balance	$ 2,996.17

ANALYSIS OF RECEIPTS

January 1 to December 31, 1949

Dues:	1948	$ 602.00
	1949	11,470.50
	1950	9,220.25
Volumes:	1948	225.50
	1949	3,522.09
	1950	784.00
Sales:	Publications	6,490.97
	Preprints	357.70
	Reprints	2,788.60
	JOURNAL	3,192.55
	Cathodic Protection	62.00

ANALYSIS OF RECEIPTS (*Continued*)

Modern Electroplating	1,330.46
Thompson Monograph	69.90
Deutschen Bunsengesellschaft	421.00
Faraday Society	2,235.59
Sustaining Memberships	6,200.00
Conventions	1,259.10
Emblems	84.20
Corrosion Division	5,080.50
Japanese-Korean Publication Rights	100.00
Advertising—JOURNAL	58.80
Interest on Savings Accounts	65.94
Total	$55,621.65

ANALYSIS OF DISBURSEMENTS

January 1 to December 31, 1949

Furniture and Office Equipment		$ 405.06
Publication Expenses:		
JOURNAL		$15,401.53
Modern Electroplating		1,185.00
Cathodic Protection		2,129.57
Volume 92: Work and Materials		4,985.96
Traveling Expenses (Publication)		227.19
Reference Books (Publication)		126.00
Publication Committee		190.00
Reprints: Volume 91		553.64
Volume 93		100.24
Volume 94		269.01
Volume 95		1,606.09
Volume 96		145.93
		$26,920.16
General Expenses:		
Salaries, Full-Time Employees		$15,720.91
Wages, Part-Time Employees		3,340.15
Stationery and Supplies		1,278.11
Office Expenses		1,225.56
Rent		1,360.00
Postage and Express		1,464.81
Conventions		1,215.31
Audit		160.00
Prizes		600.00
Certificates and Emblems		32.88
Faraday Society		2,848.00
Local Sections: Cleveland		123.00
Detroit		90.50
India		25.00
Metropolitan		193.00
Philadelphia		50.00
Electrodeposition Division		50.00
		$29,777.23
		$57,102.45
Excess Expenditures over Income		$ 1,480.80
Accounted for as follows:		
Surplus (Reduction)		$ 1,075.74
Furniture and Office Equipment		405.06
		$ 1,480.80

Treasurer's Report for 1949

Canadian Future Convention Fund

The Canadian Bank of Commerce, Toronto	
Balance, 1/1/50	$1,104.20

Corrosion Division Fund

Corn Exchange Bank, 1/1/50	
USA Savings Bonds Series F (earmarked in safe deposit box)	$10,471.37

Columbus Convention Committee Fund

Corn Exchange Bank, 1/1/50	
USA Savings Bonds Series F (earmarked in safe deposit box)	$300.00

Columbus Rotating Convention Fund

Corn Exchange Bank, 1/1/50	
USA Savings Bonds Series F (earmarked in safe deposit box)	$100.00

Edward Weston Fellowship Fund—for 1949

Weston Fund Total Balance, Jan. 1, 1949		$2,826.98
Central Hanover Bank & Trust Co.		
Total Balance Jan. 1, 1949		1,342.57
Credit: Interest on bonds and other accruals		320.33
		1,662.90
Debit: Commissions and Attorney Fees	20.39	
M. T. Simnad—Fellowship	500.00	520.39
Total Balance Jan. 1, 1950		1,142.51
National City Bank		
Income Balance Jan. 1, 1949	500.00	
M. T. Simnad Fellowship	500.00	
Income Balance Jan. 1, 1950		0.00
Seamen's Bank for Savings		
Income Balance Jan. 1, 1949	984.41	
Interest for 1949	17.29	
Income Balance Jan. 1, 1950		1,001.70
Weston Fund Total Balance, Jan. 1, 1950		$2,144.21

Joseph W. Richards Memorial Fund—for 1949

Balance, January 1, 1949	$3,591.14
Withdrawals: O. W. Storey, Oct. 6, 1949	50.00
	3,541.14
Interest for 1949	71.68
Balance, January 1, 1950	$3,612.82

CENTRAL SAVINGS BANK
Broadway at 73rd Street, New York, New York

Roeber Research Fund—for 1949

Balance, January 1, 1949	$4,907.51
Interest for 1949	98.63
Balance, January 1, 1950	$5,006.14

EAST RIVER SAVINGS BANK
Amsterdam Ave. at 96th Street, New York, New York

Treasurer's Report (*Continued*)

Edward Goodrich Acheson Fund—for 1949

Capital Fund Securities —Jan. 1, 1950*

$5,000.00 U.S.A. Savings Bond Series F, no interest; due 10/1/53. Registered.
10,000.00 U.S.A. 2½% Savings Bond Series G due 11/1/54. Registered.
2,000.00 Pennsylvania Railroad Co. 3¼% General Mortgage Bond, Series F. Due 1/1/85.
2,000.00 American Telephone & Telegraph Co. 2¾% Debenture due 10/1/75.
13 shares American Can Co. 7% Cum. Pfd.
14 shares Corn Products Refining Co. 7% Cum. Pfd.
10 shares Eastman Kodak Co. 6% Cum. Pfd.
10 shares Ingersoll Rand Co. 6% Cum. Pfd.
25 shares International Harvester Co. 7% Cum. Pfd.
20 shares National Lead Co. Class A 7% Cum. Pfd.
1 Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Participating Certificate, Series 2-7165 Bond & Mortgage. Only remaining asset is General Claim.
1 Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Series 3-6902 due 3/1/38. 5½%.
1 Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Certificate in Bond & Mortgage of Chatsworth Gardens Corp. Series 6-6972 Certificate #296. Only remaining asset is General Claim against the former guarantor.

* Guaranty Trust Company of New York, *Custodian*
Fifth Avenue at 44th Street, New York 18, New York

Balance, January 1, 1949		$2,662.06
Guaranty Trust Company		
Income Balance, January 1, 1949		1,984.39
Receipts: Recovery from mortgage	$4,750.00	
Dividends plus interest	994.48	5,744.48
		7,728.87
Withdrawals: Purchase of Pfd. Stk.	4,710.67	
Custodian charges	55.00	4,765.67
Income Balance, January 1, 1950		2,963.20
East River Savings Bank		
Principal Funds Balance, January 1, 1949		677.67
Interest		13.61
Principal Funds Balance, January 1, 1950		691.28
Acheson Fund Total, January 1, 1950		$3,654.48